Removing SERS Memory Effects in Plasmonic Superlattices

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The development of continuous monitoring systems requires in situ sensors that are capable of screening multiple chemical species and providing real-time information. Such in situ measurements, in which the sample is analyzed at the point of interest, are hindered by underlying problems derived from the recording of successive measurements within complex environments. In this context, surface-enhanced Raman scattering (SERS) spectroscopy appears as a non-invasive technology with the ability of identifying low concentrations of chemical species, as well as resolving dynamic processes under different conditions. To this aim, the technique requires the use of a plasmonic substrate, typically made of nanostructured metals such as gold or silver, to enhance the Raman signal of adsorbed molecules (the analyte). However, a common source of uncertainty in real-time SERS measurements originates from the irreversible adsorption of (analyte) molecules onto the plasmonic substrate, which may interfere in subsequent measurements. This so-called "SERS memory effect" leads to measurements that do not accurately reflect varying conditions of the sample over time. We introduce herein the design of plasmonic substrates involving a non-permeable poly(lactic co-glycolic acid) (PLGA) thin layer on top of the plasmonic nanostructure, toward controlling the adsorption of molecules at different times. The polymeric layer can be locally degraded by irradiation with the same laser used for SERS measurements (albeit at a higher fluence), thereby creating a micrometer-size window on the plasmonic substrate available to molecules present in solution at a selected measurement time. Using SERS substrates coated with such thermolabile polymer layers, we demonstrate the possibility of performing over 10,000 consecutive measurements per substrate, as well as accurate continuous monitoring of analytes in microfluidic channels and biological systems.

REFERENCES

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FIGURES
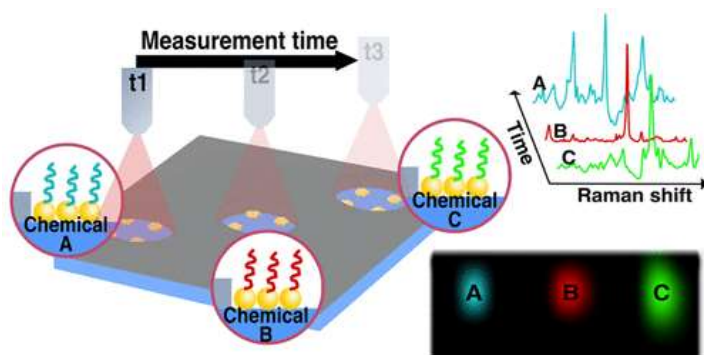
Figure 1: Schematic view of the use of an PLGA-covered plasmonic substrate for sequential SERS measurements, upon localized PLGA removal by photothermal heating.