



SERS detection of chemical contaminants in food and drinking water based on Au decorated, laser induced periodic surface structures elaborated in air and vacuum

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Food and drinking water safety is paramount in global public health systems, and the safeguard on chemical contaminants with deep implications for human health is a continuous challenge. Surface Enhanced Raman Scattering (SERS) offers a viable platform to respond to such a demand, and sensitivity improvements and elaboration of novel substrates are continuously required.

Here we report on the functionalization with Au NPs of low spatial frequency, laser induced periodic surface structures (LIPSS) generated on Si for the elaboration of SERS substrates devoted to the detection of chemical contaminants in food and drinking water. LIPSS were generated by irradiating commercial n-type Si (111) samples (resistivity in the 15-50 Ω cm range) with pulses of ~ 200 fs duration at a wavelength of ~ 1030 nm both in air at atmospheric pressure, and in a vacuum of 10^{-2} mbar. Then, Au NPs were deposited on both types of samples by magnetron sputtering. The morphological features of the processed Si samples were analyzed using Scanning Electron Microscopy, Atomic Force Microscopy and Confocal Microscopy.

The SERS response of the substrates was investigated by detecting diverse food and environmental contaminants, such as: microcystin-LR (MC-LR), a hepatotoxic cyanotoxin from algal blooms with severe health risks (chronic liver damage and carcinogenesis) at a concentration larger than 1 $\mu\text{g/L}$; malachite green (MG), an illegal aquaculture antibiotic with carcinogenic and mutagenic effects; 4-hydroxybenzoic acid (4-MBA), prevalently used in processed baby foods that disrupts endocrine function and promotes inflammatory pathologies; rhodamine B (RhB), an food dye illegally used in food products with significant carcinogenicity through subcutaneous sarcoma formation. Our findings address a very good performance of the Au decorated, Si LIPSS as a SERS platform with the surface structures elaborated in air outperforming the ones formed in vacuum, demonstrating high sensitivity in food contaminants detection, and achieving a limit of detection (LoD) as low as 10^{-12} M for MG and other prohibited additives. This outcome addresses Au-decorated, fs Si-LIPSS generated in ambient conditions as a viable approach to fabricate high performance SERS substrates and highlights the critical influence of the processing environment on the formation of nanostructures with enhanced plasmonic response.