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Metal-coated microsphere arrays: versatile nanofabrication platforms for plasmon-enhanced optical spectroscopy

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Metal-coated microsphere arrays (MCMA), consisting of metal films deposited over dielectric (polymer, SiO_2) colloidal microspheres, represent a class of plasmonic crystals with proven capabilities as substrates for surface enhanced optical spectroscopy (Surface Enhanced Raman Scattering - SERS, Surface/Metal-Enhanced Fluorescence - SEF/MEF) or sensing based on Localized Surface Plasmon Resonance (LSPR) [1,2]. Their ability to amplify the intensity of Raman scattering or fluorescence emission of molecules relies on excitation of both localized and propagative surface plasmons. By physical/chemical processing of the underlying polymer microsphere arrays various variations of the nano/microstructured metal films can be achieved, which in turn allow to modulate the plasmonic response [3]. Due to their relatively easy fabrication and tunable optical response [4], MCMA are versatile candidates for many practical applications as optical molecular sensors.

Here, some of our recent results concerning fabrication of nanostructured plasmonic surfaces, based on colloidal microsphere arrays are presented: metal-coated microspheres, metal-coated plasma-etched microspheres, linear metal-coated microsphere arrays, patterned polymer films obtained by etching through the colloidal microsphere mask. Optical reflectance/transmittance measurements, together with Finite-Difference Time-Domain (FDTD) simulations are employed for understanding the optical behaviour of these structures, and its dependence on structural parameters. Specifically, we evidence the impact of sphere size, metal films thickness and fine morphology on the transmittance, reflectance and absorbance of MCMA, or polarization-sensitive behaviour of linear MCMA. Then, the SERS efficiency of these MCMA is analyzed and correlated to the optical response, highlighting the routes towards optimizing SERS. Moreover, we use MCMA to develop plasmonic electrodes, for use in Electrochemical SERS (EC-SERS) applications, or integrate them in microfluidic devices for in-flow SERS detection. The use of MCMA as substrates for more specialized spectroscopic techniques such as Surface-Enhanced Coherent Anti-Stokes Raman Scattering (SECARS) is also explored. These results demonstrate the utility of MCMA as platforms for fundamental plasmonics studies, but also for developing practical applications in optical molecular sensing.

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