All-Dielectric SERS with T-Rex Beads: Recent Advances and Perspectives

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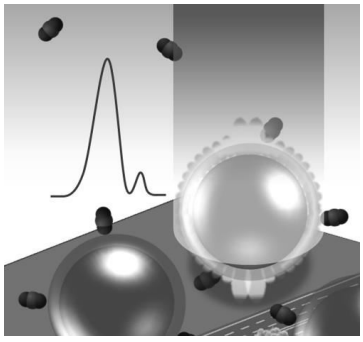
All-dielectric nanostructures are intensively investigated for developing analytical platforms based on enhanced vibrational spectroscopy. Surface Enhanced Raman Scattering (SERS) can take full advantage of high-refractive index dielectrics to overcome most of drawbacks related to the use of plasmonic metals. In particular, the strong concentration of the local electromagnetic field, which is at the basis of conventional SERS effect, can severely alter the system under analysis, for example through the promotion of plasmon-assisted reactions or photothermal degradation of the analytes. Either denaturation or passivation of specific functional groups are further major issues to be taken into account, primarily in SERS experiments on biological samples. As a result, high sensitivity achieved by conventional, metal-assisted SERS is often undermined by low reproducibility. On the other hand, high-refractive index dielectric materials represent plasmon-free, low-loss alternatives, which can be useful for in-situ monitoring of chemical and biochemical processes under real-working conditions.
For example, core/shell SiO_2/TiO_2 (T-rex) or hollow TiO_2 spheres (T-horex) have been recently utilized to detect organic pollutants and small peptides, as well as to monitor their reactions with high spatial control and reproducibility. These core/shell colloids combine evanescent fields resulting from total internal reflection and multiple scattering of light at the sphere-to-sphere interface to amplify the optical path length and extract more Raman photons.[1] These spheres can also be assembled to form extended colloidal crystals, adding further benefits coming from analyte pre-concentration.[2]
Here a few examples of recent advances in the applications of T-rex beads for SERS purposes will be discussed. In the the first example of a synergistic combination of T-rex colloids with synthetic receptors for SERS-based (bio)diagnostics. Tetraphosphonate cavitands, molecular receptors capable of binding N-methyl ammonium salts with extremely high selectivity, were used in a series of proof-of-concept experiments addressed to unambiguously detect methylated ammonium salts in the absence of any distinctive spectral fingerprints.[3] These results provide an experimental guideline to design new SERS assays for epigenetic diagnostics.
In a second example, the T-rex beads were tested for achieving the plasmon-free detection of CO_2 in both air and solvents. The dependence of SERS activity on Mie-type resonances was investigated through a systematic comparison of experimental data and numerical simulations.[4] Future challenges in the use and integration of T-rex beads and related high-refractive index dielectric interfaces in analytical platforms for studying surface reactions will be also discussed.



References

[1] Alessandri. I. *J. Am. Chem. Soc.* **135**, 5541 (2013).
[2] Alessandri, I., Depero. L. E., *Small* **10**, 1294 (2014).
[3] Alessandri, I., Biavardi, E. Gianoncelli, A. Bergese, P. Dalcanale E. *ACS Appl. Mater. Interfaces.* in press, doi:10.1021/acsami.5b08190.
[4] Bontempi, N., Carletti, L., De Angelis, C., Alessandri I. *Nanoscale*, **8**, 3226 (2016).