Layer-by-Layer assembly of nanocomposite colloidal probes for Raman-based detection of biomolecules

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Self-assembly of colloidal noble metal nanoparticles into macroscopic one, two, and three-dimensional arrays either flat or curved substrate is very promising approach, that is to developing sensors based on plasmonic effect. Layer-by-Layer (LbL) deposition is established method for fabrication of multicomponent structures on the solid support in the nanoscale. We applied in this work LbL approach to fabricate nanoplasmonic sensors based on gold nanoparticles adsorbed over carbon nanotubes network and also introduced those into pores of calcium carbonate ($CaCO_3$) microparticles. Roughened structure of developed colloids allowing us to use them as detectors of molecules in Raman experiments based on surface enhancement Raman scattering effect (SERS). Today SERS is one of powerful analytical tool, especially in term of label-free purposes. Compare with fluorescence imaging SERS overcomes photobleaching and provides highly detailed molecular information. Since the discovery of surface enhanced Raman scattering novel platforms have evolved and various approaches to SERS substrates have been introduced.

Currently, we achieved remarkable high Raman scattered signal from probe based on silica core coated with carbon nanotubes subsequently functionalized with gold nanoparticles aggregates. Functionalized carbon nanotubes provide easy localization at extremely low laser powers and increased roughness necessary for highly efficient SERS amplification [1]. Upon intracellular incorporation probes significantly enhance molecular fingerprints of biomolecules commonly found inside NIH3T3 fibroblast and enable fast acquisition rates at laser powers completely harmless to living cells (Fig. 1). Remarkable increase of SNR due to SERS allows visualization and detection of biomolecules. The Raman probes developed in this work can be ubiquitously applied for molecular imaging and sensing in cells and tissues.

We continue our study for assembling of gold nanoparticles within pores of calcium carbonate microparticles. Porous calcium carbonate microparticles exhibited superior performance in comparison to smooth silica particles. Porosity which can be linked to adsorption of particles is identified as a key mechanism leading to an increased nanoparticle adsorption and enhanced label-free Raman based detection [2]. Using these particles, label-free detection of important biomolecules such as glucose (Fig. 2) and bovine serum albumin is demonstrated at concentrations of nM–μM levels. Such an approach is attractive for developing biomarker sensing at concentrations corresponding to healthy and diseased individuals.

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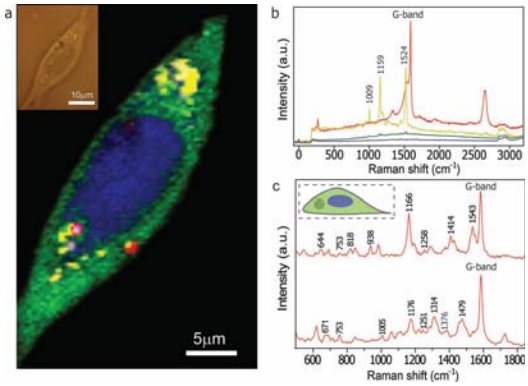

Fig. 1. Raman spectroscopic imaging of a living fi broblast cell with incorporated colloidal probes. (a) Linear combination of the averaged single spectra b) Characteristic for cell compartments (green-cytoplasm, blue-nucleus, yellow-carotenoids) and gold-nanoparticle- SWCNT functionalized colloidal probes (red). (c) Intracellular SERS signal recorded at the surface of the probe.

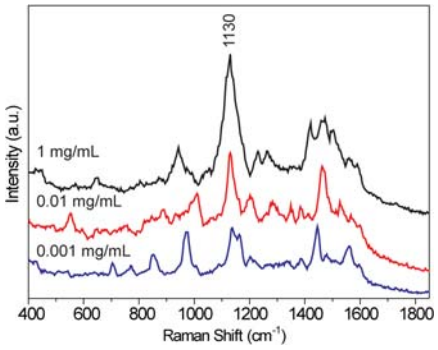

Fig.2 SERS spectra of D-Glucose molecules with varying concentration. The characteristic peak at 1130 1/cm is pointed out. All measurements were made using 785 nm laser (10 mW).