Attomolar Sensnig by Liquid-Interface SERS Using 3D Glass Microfluidic Chip Fabricated by Hybrid Femtosecond Laser Processing

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Surface enhanced Raman scattering (SERS) is a multidisciplinary trace analysis technique based on plasmonic effects. The development of SERS microfluidic chips has been exploited extensively in recent years impacting on applications in diverse fields. However, despite much progress, the excitation of labelfree molecule is extremely challenging when analyte concentrations are lower than 1 nM due to the blinking SERS effect. In this presentation, a novel analytical strategy which can achieve detection limits at aM level is proposed. This super high sensitivity is realized due to the use of a glass microfluidic chip that generates an analyte air-solution interface on the SERS substrate in the microfluidic channel, whereby the analyte molecules aggregate locally at the interface during the measurements, hence the term liquid-interface assisted SERS (LI-SERS). The microfluidic SERS chips were fabricated using hybrid femtosecond laser processing consisting of femtosecond laser assisted chemical etching, selective metallization and metal surface nanostructuring [1]. The nanostructuring for noble metal SERS substrate in the microfluidic chip was performed based on femtosecond laser induced periodic surface structure (fs-LIPSS). To generate homogenous periodic structure on SERS substrate, laser parameters such as pulse energy and repetition rate for laser irradiation wavelengths of 515 and 1030 nm were optimized. To perform the LI-SERS, LIPSS with an average period of 140 nm and an average gap of 43 nm was fabricated by 515 nm fs-laser. The novel LI-SERS technique can achieves an analytical enhancement factor of 1.5×10^{14} providing a detection limit below 10⁻¹⁷ M (<10 aM). Due to the Marangoni convection induced by photothermal effect at the liquid interface, vortex was formed near Raman excitation laser spot which forced the analyte to enter into the hotspots of SERS substrate. This transportation of analytes accelerated the local deposition in laser focal spot and significantly promoted the extraordinary increment of SERS intensity.



Figure 1. a) Schematic of LI-SERS using the microfluidic SERS chip and b) LI-SERS results for various concentrations of R6G.

Reference

1. S. Bai, D. Serien, A. Hu et al. Adv. Funct. Mater. 2018, 1706262.