A nanofiltration technique for analyte extraction from complex matrix and surface enhanced Raman spectroscopy based sensing

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A nanofiltration technique for analyte extraction from complex matrix and surface enhanced Raman spectroscopy based sensing

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Abstract

Our novel proof-of-concept centrifugal microfluidics sensing platform (Fig.1), allows to perform fast and facile purification (nanofiltration) of the complex sample by incorporating inertial (centrifugal) and capillary forces. Furthermore, integrated in the platform, highly uniform Au capped Si nanopillar (NP) substrates for surface enhanced Raman spectroscopy (SERS) are capable to detect analyte molecules in trace amounts [1]. However, in most of the cases SERS based sensing applications are accompanied with complicated sample manipulation and external purification steps. This can be addressed to various experimental difficulties of SERS based measurements when handling real-life complex samples. Therefore, we believe that combination with the nanofiltration technique would sufficiently increase sensitivity and applicability of SERS based sensors. In addition to that, the nanofiltration of the sample and SERS based sensing of analyte is carried out on the same chip (Au NP surface) which provides robustness to the platform.

The microfluidic procedure for nanofiltration of the complex medium is schematically presented in Fig1a-d. First, the sample is injected to the loading chamber of the microfluidic unit (Fig.1a). Then, the disc is accelerated to rotation frequency of 47.5 Hz and the sample is transferred to the sensing chamber immersing half of the NP substrate (Fig.1b). At this step nanofiltration of the sample is performed. In Fig.1e real time images of SERS chip during the purification step are shown. Gradual coverage of SERS chip with purified sample can be clearly observed. The liquid front at the immersion boundary is illustrated in Fig.1f. To achieve such liquid configuration and promote wetting of SERS chip, addition surfactants which increase capillary (adhesive) force of sample towards Au NP structures should be considered. Lastly, after the nanofiltration step, the liquid is removed my adjusting the rotational frequency to 25 Hz (Fig1c, d).

Melamine is a nitrogen rich compound which usually used in polymer industry due to its heat resistivity. Recent incidents showed that melamine can be illegally added to food and feed products to increase apparent protein content. Consumption of melamine-contaminated products can cause serious health issues like kidney disease [2, 3]. Commonly applied detection techniques for food content monitoring are high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), mass spectrometry (MS), etc. [4]. Time consuming measurement and sophisticated sample preparation steps are some of the general drawbacks of these methods [5]. Moreover, lack of possibility to perform in-field analysis is another limiting factor for food quality controls. Therefore, there is an increasing interest and need in establishment and development of new sensing and sample treatment approaches [4].

We testified the validity of our sensing platform for a well-known application, detection melamine in milk samples. To increase the wetting properties, milk solutions were diluted with acetone to 100:15 ratio. Furthermore, to protonate melamine molecules, hydrochloric acid was added (1.5 wt% in total milk solution). The assessment of nanofiltration efficiency can be done by comparing surface morphologies of chip on immersion and wetted areas (Fig.2). Raman spectra recorded from wetted chip containing different concentrations of melamine and the calibration curve is presented in Figure3.

Hereby, we demonstrated SERS based sensing of Melamine in centrifugal microfluidic platform as comparably cheap, fast and facile approach without implementation of external sample purification steps.

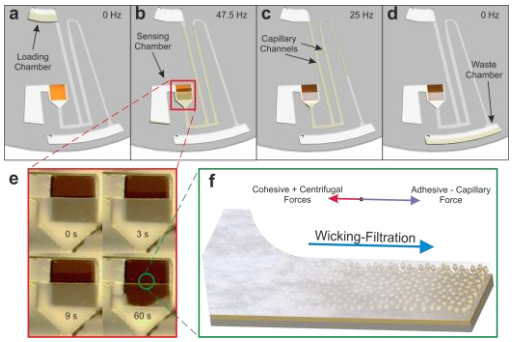

Figure 1. (**a-d**) Step by step schematic illustration of sample purification procedure in centrifugal microfluidics platform. In (**a**) initial condition of the disc is represented, the sample is located in loading chamber. (**b**) depicts the purification step in which disc is accelerated to 47.5 Hz and the sample is transfered to the sensing chamber through channels. (**c**, **d**) Illustrates the sample removal step which occurs at 25 Hz. With the help of capillary channel and centrifugal force, sample is transfered to waste chamber. (**e**) Real-time images of SERS chip captured during the purification step. (**f**) Graphical representation of nanofiltration phenomenon at the immersion boundary.

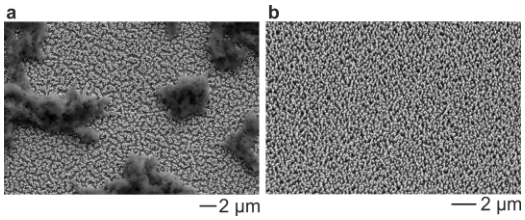

Figure 2. (**a**) SEM image of SERS chip in the immersion region. (**b**) Comparative SEM image obtained from a region where the sample was soaked ("purified region").

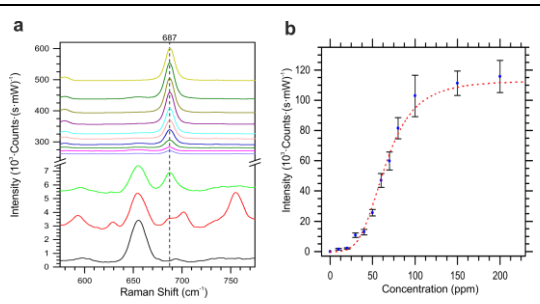

Figure 3. (**a**) Averaged SERS spectra of various melamine concentrations in milk acquired from purified region. (**b**) Calibration curve plot per data acquired from (**a**). The data fitted to Langmuir absorption model (red).

[1] K. Wu, T. Rindzevicius, M. S. Schmidt, K. B. Mogensen, A. Hakonen, and A. Boisen, J. Phys. Chem. C 119 (2015) 2053–2062.
[2] Kim Ansoon, et al., Analytical chemistry 84 (2012) 9303-9309.
[3] Chan E. Y. Y., S. M. Griffiths, and C. W. Chan., The Lancet 372 (2008) 1444-1445.
[4] Liu, Y., et al., Journal of Zhejiang University-Science B 13 (2012), 525-532.
[5] Lin M., et al., J. of food science 73 (2008) 129-134.