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## Challenges in the integration of silicon SERS substrates into a polypropylene injection moulded microfluidic chip

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Integration of sensors into microfluidic systems is often challenging,<sup>1</sup> especially when incorporating fragile and sensitive elements such as silicon or glass based sensing units. The major challenge is to achieve leakage-free systems without compromising sensor performance. There are several approaches for integration of a wide variety of surface enhanced Raman scattering (SERS) substrates. Various methods were reported, based either on the fabrication of active nanostructures inside the microchannels, or on the combination of a SERS substrate with a PDMS microstructured cap.<sup>2</sup> The SERS substrate used in this work is a silicon chip with a nanostructured surface of gold-capped nanopillars, previously developed by Schmidt et al.<sup>3</sup>

In our group we are currently working on the adaptation of an assay combining liquid-liquid extraction (LLE) and SERS sensing for quantification of bacterial metabolites<sup>4</sup> into microfluidics. In the LLE process organic solvents (e.g. dichloromethane) are needed, which are incompatible with the polymers commonly used in the development of microfluidic devices (e.g. PDMS, PMMA, TOPAS). Polypropylene (PP) is a suitable chemically resistant thermoplastic polymer, although not compatible with traditional polymer bonding procedures (e.g. thermal, solvent-assisted bonding). Ultrasonic welding (UW) is a thermal fusion process where frictional heat is locally delivered through energy directors at the interface of the two polymeric parts to be melted together.<sup>5</sup> It is a fast alternative to glue or heat based bonding, therefore particularly suitable for solvent-resistant polymers, such as PP. However, high energy is delivered to the polymer parts, which could cause damage to incorporated fragile sensing elements.

In this work we present various approaches for the integration of our silicon based SERS substrate onto a PP microfluidic platform for automated LLE. The fluidic platform was fabricated with injection molding and bonded through UW. Solvent-assisted gluing of the SERS chips was not feasible, therefore mechanical clamping was considered. As an adhesive-free approach, chemical contamination of the SERS substrate due to glue degradation is avoided. However, mechanical clamping (Figure 1) was not suitable, since the vibrational energy from the UW was easily transferred to the SERS chip when clamped to the walls of the chamber (data not shown).

As a next step, epoxy glue and double-sided adhesive tape were tested. Smaller SERS chips (2 x 4 mm) were glued in the middle of the sensing chambers to avoid any contact with the chamber walls and breakage due to the UW. As shown in Figure 2, the double-sided tape (b) proved more effective than epoxy glue (a) for damping vibrations from the UW. However, compared to the typical surface of a SERS chip (Figure 3(a)), the tape-glued chip still showed damage towards the edges (Figure 3(b)). A comparison between the SERS signal collected from a chip after integration and one without integration (Figure 4) indicates that the integration was successful. The integrated SERS chip gave lower signal, but the absence of interfering peaks (e.g. from degradation of double sided tape) and the presence of a significant signal from the substrate even after integration indicate possibility of effective sensing on the platform. We are currently evaluating other possibilities for better counteracting the effect of UW while achieving a solvent-resistant integration, such as the application of inert UV curable glues. As a result of successful integration, we will demonstrate the detection of bacterial metabolites on the platform.

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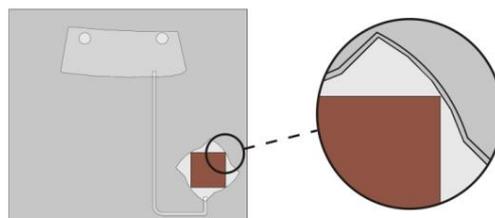


Figure 1: detail of microfluidic design with a 4 x 4 mm SERS chip clamped in a microfluidic windmill-like chamber. Mechanical clamping is achieved by twisting the chip with tweezers until it is secured. (inset) energy directors for ultrasonic welding around the microfluidic chamber.

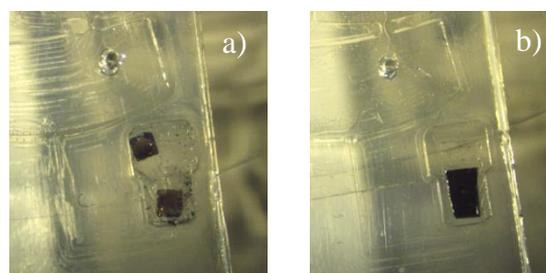


Figure 2: (a) SERS chips glued with epoxy glue and (b) with double sided tape after ultrasonic welding of the microfluidic chip.

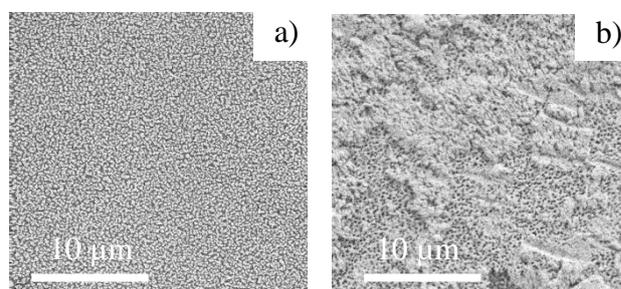


Figure 3: (a) top view of the typical surface of a SERS chip; (b) damaged nanostructures at the edge of a SERS chip glued with double-sided tape after ultrasonic welding.

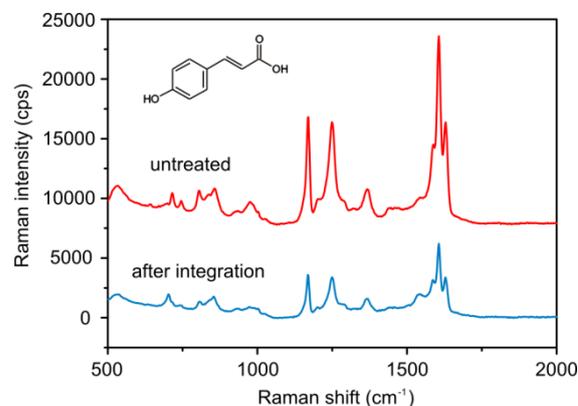


Figure 4: SERS signal of 50 µM p-coumaric acid in DCM from an untreated SERS chip (red) and after integration in the microfluidic system (blue). Each spectrum is the average of 48 points, collected with a DXRxi Raman Imaging Microscope at 780 nm with a laser power of 2 mW, 3 x 0.05 s, 10x lens, 50 µm slit. The spectra were arbitrarily shifted for ease of representation.