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# Transparent polymer-based SERS substrates templated by a soda can

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## ABSTRACT

This paper demonstrates the reproducible fabrication of transparent Surface Enhanced Raman Scattering (SERS) substrates, fabricated by employing an aluminium soda can to template nanostructures on a flexible thermoplastic polymer surface, followed by deposition of a silver over layer. Electron microscopy and finite element modelling simulations strongly suggested the SERS response arose at regions of high electromagnetic field strength occurring between metallic clusters following illumination by monochromatic radiation. The sensors exhibited rapid, quantitative and high sensitivity, for example, $5 \times 10^{-10}$ M (204 pg/mL) crystal violet detection in 10 min using a simple drop and dry method. We also show detection of glucose employing a chemically modified silver surface bearing a pre-deposited SAM layer. Furthermore, the transparent substrates permitted back excitation and collection through the substrate with corresponding spectra exhibiting clear and well-defined spectral SERS peaks. Finally, we present the detection of trace amounts of melamine in complex media solution (milk and infant formula). We benchmark the sensor performance using commercial analytical instrumentation (MS-MS) and show comparable sensitivity between the SERS substrates and MS-MS.

## 1. Introduction

In recent years, advances in nanotechnology and nanofabrication techniques have enabled significant enhancement in a variety of analytical sensor devices. These devices, employing electronic [1–3], electrochemical and optical [4–6] detection methods, have provided quantitative and sensitive measurements. However, within the environmental and security sectors, highly sensitive sensing alone is not enough; rapid on-site molecular identification is also essential. One analytical approach that addresses these criteria is surface enhanced Raman spectroscopy (SERS) [7,8] which provides both a spectral molecular fingerprint and allows for trace analyte detection; with the potential for single molecule sensitivity. [9–14] SERS is thus emerging as a powerful technique for remote chemical [15] and biological sensing applications [16].

SERS enhancement occurs at nanostructured plasmonic surfaces following illumination with monochromatic radiation and results from (i) an increase in local electromagnetic field strengths of localised surface plasmons (in nanogaps between metal clusters called "hot spots") and (ii) chemical resonant energy charge transfer [17–20]. For these processes to occur, substrates must be capable of supporting plasmonic modes (collective oscillations of metal electrons) and have a nanostructured rough surface with well-defined gaps in the region of 10–100 nm between metallic clusters (to conserve momentum). To this end, fabrication of SERS substrates using top-down approaches including: lithography techniques (Electron beam [21,22] and nanoimprint [23] lithography's), laser etching [24], film deposition (sputtering, metal evaporation, atomic layer deposition) [25,26] and templating (using anodic aluminium oxide [27], masks [25] or molds [28]) as well as bottom-up approaches including chemical synthesis [29], colloid aggregation [30] and self-assembly [31,32] of metal nanoparticles [33,34], nanowires [2,28], nanospheres [33,35,36], nanorods [37–39], nanotubes [27], nano-triangles [40], nano-urchins [41] and/or nanoshells [42] have been reported.

While these approaches are elegant and are attractive in research environments for their large SERS enhancement; they are limited in that they may be expensive, time consuming, and can require complex fabrication approaches which may have low throughput. Consequently, a critical challenge inhibiting the uptake of SERS for sensor applications is the lack of scalable and reproducible fabrication approaches compatible with mass manufacturing. To address this challenge, we have developed a

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templating approach employing "inherent" nanostructured aluminium (Al) masters (obtained from commercial soda drink cans) to template low-cost polymer replicates which are subsequently coated with a thin (30 nm) silver (Ag) layer. These transparent polymer substrates offer a number of advantages: (i) the simple manufacturing approach is scalable offering the potential for low-cost fabrication and thus widespread uptake and applicability. (ii) The fine metallic nanostructures provide SERS hot spots upon optical excitation. (iii) The substrates are transparent and thus are compatible with back excitation and collection allowing measurement in liquid environments to be undertaken. ((iv) the flexible substrates may be easily integrated in-line or on-line adding to the suite of spectroscopic process analytical techniques used in smart manufacturing 4.0 approaches. (v) Finally, the sensor may be chemically modified to widen the range of molecules that may be detected.

To explore the versatility of our as-fabricated SERS substrates towards real world applications, e.g., environmental monitoring and food security, a variety of different target molecules were selected and analysed. Initially, 4-aminothiophenol (4-ABT) and crystal violet (CV) [43] were selected to characterise SERS effect and allow comparison with the published literature. We show highly sensitive detection of crystal violet with a measured limit of detection of 204 ng/L (204 parts per trillion, equivalent to $5 \times 10^{-10}$ M). Malachite green was also selected as this and other trimethyldiamine dyes are used indiscriminately as antimicrobials in aquaculture, despite the reports of causing serious toxic, carcinogenic and mutagenic effects in mammalian cells [44,45]. Consequently, the presence of trimethyldiamines are now tightly controlled with (MRL) set at 2 µg/L (2 ppb) in water [46]. Glucose was analysed by first capturing the molecule on a substrate pre-modified with a mixed thiol monolayer in a manner similar to that reported by the Van Duyne group [47]. Finally, melamine was selected as it now requires regular monitoring due to its previous use to give a false appearance of high protein levels in milk [48]. Melamine MRLs are now set at 2.5 ppm for food products (including milk) and 1 ppm in infant formulae [49]. We demonstrate detection of low concentrations of melamine (100 ppb) spiked into both milk and infant formula solutions (without sample pretreatment), using a drop-and-dry sampling technique with a total analysis time of 10 min and benchmark these results using mass spectroscopy (MS-MS).

## 2. Material and methods

### 2.1. Material and reagents

Polystyrene (PS), 4-aminothiphenol (97%), polyvinylidene fluoride (PVDF), crystal violet (<90% dye content), malachite green, benzocaine, 1-decanethiol, mercaptohexanol, glucose and melamine and analytical grade solvents were purchased from Sigma-Aldrich (Dublin) and used as received. Polydimethylsiloxane 184 silicon elastomer and curing agent were purchased from Sylgard®. PTFE syringe filters (0.45 µm) were purchased from Lab Unlimited (Dublin). Full-fat milk and infant formula were purchased from a local supermarket. 4-aminothiophenol (4-ABT), 1-decanethiol (DT) and mercaptohexanol (MH) were prepared by dissolving in ethanol. All standards of crystal violet (CV), melamine, and glucose were prepared as required, using deionized water (18.2 MΩ.cm ELGA Pure Lab Ultra systems) and a serial dilution

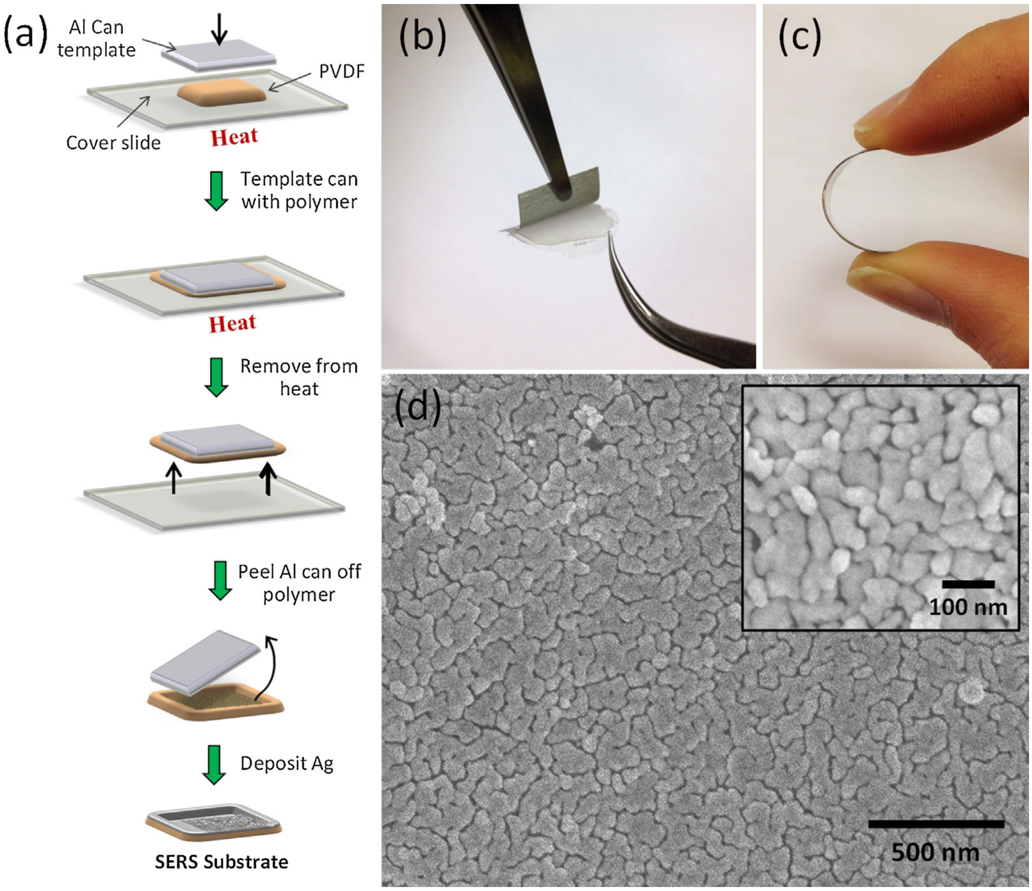

**Fig 1.** (a) Schematic outlining the fabrication of the Ag-covered nanostructured PVDF SERS substrates. (b) Image of Al easily peeling off the templated polymer. (c) Flexible PVDF substrate. (d) SEM image of a PVDF substrate template with the nanostructured Al with 30 nm of Ag deposited over the surface. Inset: Substrate at a higher magnification.