Nanostructured metallic thin films for sensing applications

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Nanostructured metallic thin films are key components of several proposed devices that promise to translate the discoveries of nanoscience and deliver technological solutions to issues ranging from energy security, affordable healthcare sensors, to robust digital storage etc. The advancement of Laser technology has enabled wide-spread use of Raman spectroscopy, with the main advantage over conventional vibrational (IR) spectroscopy being its insensitiveness to the presence of water vapour, rendering it an ideal tool for environmental sensing applications. Surface Enhanced Raman Spectroscopy (SERS) is a label-free, point-of-use Raman technique capable of exhibiting high selectivity, and sensitivity. The surface enhancement comprises of an electromagnetic effect and a charge-transfer effect. The nanostructured metallic substrate is the key factor that controls the electromagnetic effect, which is considered to be dominant factor and to be present in all situations. Therefore, significant research effort has gone into fabricating SERS substrates with characteristics like high sensitivity, signal uniformity, and reproducibility.

For most common applications, prefabricated SERS substrates are the key to commercialization. Over the last two decades, there has been rapid advancement in terms of uniformity, stability and reproducibility of silicon-based SERS substrates decorated with nanoscale plasmonic features. Flexible substrates, such as paper or plastic films, are gaining wide recognition as disposable, low-cost, SERS substrates. Paper enables pre-concentration of samples by using configurations such as dipsticks, filters, swabs, and lateral-flow platforms. Paper is also sought-after for being easily disposable by burning, which is of importance in bioanalytics.

Despite these advancements, the translation of SERS from laboratory setting to a field-setting is hindered by the inability to fabricate SERS active nanostructures on demand or store them in a scalable and economical manner. To address this issue, we fabricated silver-nanostructures *in situ* on paper by adapting our simple print-expose-develop process (see Figure 1) [1], which is based on salt-printing technique used in silver halide

photographic process, and characterized their SERS activity. Most importantly, we show that photo-exposed silver halide film retains silver in a latent but stable form under atmospheric conditions, and that immersing such silver halide films in a standard photographic developer solution for a few minutes before use generates pristine, SERS-active, silver nanostructures on demand.

In this talk, we will present salient aspects of our fabrication process involving a hP office desktop printer and discuss the results of SERS activity characterization and its use as a swab to detect pesticides on fruit peels. Finally, we will highlight the unlimited shelf-life of our paper based substrates.

Figure 1: (a) Schematic representation of the print-expose-develop cycle. (b) FESEM images of the film after printing (top panel) and after light exposure and development (bottom panel). The insets in the top-left of these images are lower magnification images showing nanostructure coated paper-fibers. The scale bars in these insets correspond to 10 μm . The lower inset in the bottom panel is a cross-sectional view of the nanostructured film. (c) XRD of the films formed on paper after printing (top panel) and after developing (bottom panel) (reproduced with permission from Parmar and Santhanam [1]).

Reference

1. Parmar, S. K.; Santhanam, V. *Curr. Sci.* **2013**, *107* (2), 262–269.