# Nanostructured Metallic Thin Films (NMTF) for Sensing and Energy Conversion

File No : EMR/2016/005343 (Ver-1)

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# Proposal

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## Proposal Details

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| **Project Title :** | Nanostructured Metallic Thin Films (NMTF) for Sensing and Energy Conversion | | |
| **Scheme :** | Extra Mural Research Funding (Individual Centric) | | |
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**Project Summary :**

Nanostructured Metallic Thin Films find applications in a wide variety of fields ranging from catalysis, electronics, energy conversion to sensing. In this proposal, we intend to build upon our recent work on inkjet printed silver nanostructures and i) optimize the morphology for swabbing-based detection of pesticide residues on fruits/vegetables, ii) develop a process based on self-limiting electrodeposition to fabricate platinum overlayer coated nanostructured thin film electrodes for PEMFC applications. The ability to detect pesticide residues in the field using SERS swabs will empower Food inspectors, consumers and also serve as quality check for the burgeoning “organic” food industry.While the ability to manufacture Nanostructured Thin Film Electrodes for PEMFCs using low-cost, roll-good processes will be a boost for PEMFC deployment in the automobile industry.

**Objective :**

• Optimizing flexible SERS substrates for pesticide detection in field-studies
• Process development for large-scale production of an ultra-low loading platinum overlayer coated nanostructured electrode for PEMFC applications

**Keywords :** Metallic Thin Films, SERS, PEMFC, Energy, Pesticide Detection

**Expected Output and Outcome of the proposal :**

A non-destructive and field-portable technique for detecting pesticides on fruits/vegetable.
A low-cost process for manufacturing electrocatalyst layers with ultra-low platinum loading.

# Other Technical Details

## 1. Origin of the Proposal:

Metallic Thin Films have been prominently used in various optical devices for centuries and are vital components in several recent optoelectronic technologies. Presently, researchers are investigating the use of Nanostructured Metallic Thin Films (NSTF) for applications ranging from energy conversion to sensors. Typically, NSTFs are fabricated from substrates prepared by physical deposition onto nanostructured templates or by dealloying of thin films. As such, these processeds incur a significant energy cost. Recently, there has been developments on using additive technologies such as printing to form NSTF from nanoparticles as building blocks. In this context, our group has developed a process utilizing an office desktop printer for fabricating silver nanowire networks on paper. The origin of this proposal is based on utilizing this process to develop products for pesticide detection based on the principle of Surface Enhanced Raman Spectroscopy (SERS) and electrocatalysts for Proton Exchange Membrane Fuel Cells (PEMFC).

## 2. Review of status of Research and Development in the subject

### 2.1 International Status:

Surface Enhanced Raman Spectroscopy (SERS) is a label-free, point-of-use spectroscopic technique capable of exhibiting high selectivity,(Li et al., 2014) based on molecular fingerprinting, and sensitivity,(Ru and Etchegoin, 2012) even unto single-molecule detection levels. SERS based sensors with applications in a wide variety of analytical(Halvorson and Vikesland, 2010; Xie et al., 2013; Gong et al., 2014; Zhu et al., 2014) or bioanalytical(Pallaoro et al., 2015) or material characterization(Azoulay et al., 2000) settings have been developed. The surface enhancement comprises of an electromagnetic effect and a charge-transfer effect. The nanostructured metal substrate is the key factor that controls the electromagnetic effect, which is considered to be dominant factor and to be present in all situations.(Sharma et al., 2012) Therefore, significant research effort has gone into fabricating SERS substrates with characteristics like high sensitivity, signal uniformity, and reproducibility.(Polavarapu et al., 2013) In the early stages of SERS development, analytes were added into silver colloidal solutions so as to sandwich molecules within 'hot spots' formed by nanoparticle flocculation, yielding high Raman signal enhancements, albeit random and transitory in nature.(Sackmann and Materny, 2006) However, for most common applications, prefabricated SERS substrates are the key for 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, either using top-down or bottom-up approaches.(Sharma et al., 2013) Flexible substrates, such as paper or plastic films, are gaining wide recognition as disposable, low-cost, SERS substrates.(Polavarapu et al., 2013) Moreover, paper enables pre-concentration of samples by using configurations such as dipsticks,(Yu and White, 2013; Webb et al., 2014) filters,(Meng et al., 2013) swabs,(Lee et al., 2010; Sivaraman and Santhanam, 2012; Gong et al., 2014) and lateral-flow,(Abbas et al., 2013; Yu and White, 2013) as well as easy integration with low-cost paper-based micro/optofluidic platforms.(White, 2011) Paper is also sought-after for being easily disposable by burning, which is of importance in bioanalytics.(Meng et al., 2013) Finally, paper is a substrate with hierarchical roughness that can lead to larger surface area serving as a platform for plasmonic interactions between multiple layers.(Ngo et al., 2012) Paper based SERS substrates have been fabricated either by depositing nanostructures using seeded growth,(Gong et al., 2014) self-assembly,(Sivaraman and Santhanam, 2012) adsorption from colloidal solution,(Ngo et al., 2012) brushing,(Zhang et al., 2014) filtration,(Zhang et al., 2015) inkjet printing,(Yu and White, 2010, 2013) physical vapour deposition,(Singh et al., 2012; Zhang et al., 2012) screen printing,(Qu et al., 2012) or by in situ formation using chemical reduction.(Volkan et al., 2005; Zhu et al., 2014) Amongst these, the use of additive drop-on-demand printing technology offers a cost-effective route for manufacturing of SERS substrates.

Polymer electrolyte (or proton exchange) membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) are energy-efficient alternatives to combustion engines for automotive(Debe, 2012) and mobile applications,(Sundarrajan et al., 2012; Joghee et al., 2015) and are on the cusp of mass-production. Significant advances have been made in PEMFC system design over the last three decades in terms of cost-reduction and structural design.(Gasteiger et al., 2005) The membrane electrode assembly (MEA), especially the electrode, is considered as 'the heart' of a PEMFC and is designed to accommodate constraints imposed by the cost of platinum used for electrocatalysis, as well as the need for efficient transport of electrons, reactants and heat. Consequently, the structure and composition of the 'electrode' has been significantly altered over the years, from utilizing platinum black films with a platinum loading of 10 $g_{pt}/cm^2$ in 1970s to present-day platinum/PGM nanoparticle coated carbon black particles (Pt/C) that use about 0.3 $mg_{pt}/cm^2$.(Costamagna and Srinivasan, 2001) The use of highly-dispersed nanoparticles on carbon black particles enables large gains in surface area for a given mass of catalyst, but concomitant durability problems due to carbon support corrosion and loss of surface area under PEMFC working conditions,(Ferreira et al., 2005; Paddison and Gasteiger, 2013; Cao et al., 2014) especially during start-up or shut down cycles have led to renewed interest in carbon-free nanostructured electrodes,(Antolini and Perez, 2011) which employ a thin coating of platinum or PGM based catalytic layer on a mesostructured conductive support.(Ge et al., 2009; Liu et al., 2009; Alia et al., 2010; Biener et al., 2011; Kloke et al., 2011, 2012; van der Vliet et al., 2012; Debe, 2013; Cheng et al., 2015; Inaba et al., 2015) Such thin film architectures can lead to reductions in platinum loadings to about 0.05 $mg/cm^2$,(Zeis et al., 2007) while reducing surface area losses due to nanoparticle agglomeration and preventing corrosion of the underlying substrate.(Debe et al., 2006)

So far, the catalyst layers have been deposited either using top-down approaches such as sputter deposition(Ge et al., 2009; van der Vliet et al., 2012)or atomic layer deposition (ALD)(Inaba et al., 2015) onto organic mesostructures that are *a priori* coated with a conductive layer or bottom-up techniques that utilize nanoporous metallic films, formed by dealloying, as a conductive substrate onto which thin platinum layers are deposited by chemical(Zeis et al., 2007) or electrodeposition(Alia et al., 2010; Kloke et al., 2011, 2012; McCurry et al., 2011)routes. The reported values of the electrochemically active surface areas (ECSA) for thin film nanostructured catalyst layers are much lower than that of conventional Pt/C layers, but their performance under PEMFC test conditions are equivalent to that of Pt/C layers, and this is attributed to enhanced specific activity associated with bulk-like polycrystalline grains as well as enhanced electrical conductivity of the catalyst layer.(Debe, 2010) Presently, the thicknesses of the metallic films used in such electrodes is of the order of 100 nm to provide macroscopic uniformity of coating and ensure electrical connectivity. However, there is scope for novel designs to further reduce platinum/PGM loading of thin film nanostructured electrodes.

## 2.2 National Status (last five years):

Several groups at various national institutes are active in the area of SERS.(Dutta et al., 2013) (Shibu et al., 2011)(Sil et al., 2013)(Chamuah et al., 2016) These studies are typically based on rigid substrates for SERS detection. Recently, a group from IIT Delhi has reported the use of flexible PDMS based plasmonic substrates for the detection of pesticide residue. (Kumar et al., 2017) Achira labs Pvt. Ltd, a Bangalore based company, in collaboration with a Canadian research group has fabricated SERS substrates on threads using traditional "zari" fabrication technique. (Robinson et al., 2015)

Synthesis of catalysts for PEMFC applications has been extensively studied by various groups in India over the last decade.(Senthil Kumar and Pillai, 2014)(Ghosh et al., 2013; Sahoo et al., 2015) Recently, a few groups have also reported on the fabrication of ultra-low platinum loaded electrodes. (Dhavale and Kurungot, 2012) (Khan et al., 2014)

## 2.3 Importance of the proposed project in the context of current status

The development of non-destructive, low-cost technologies for pesticide detection at the point-of-sale/consumption or for field-inspections is a pressing need for the food industry in particular and the agricultural sector in general. Although paper-based SERs substrates, based on inkjet printed silver/gold colloids, are available commercially (Ocean Optics), their shelf-life is limited to a few months and they are also packaged in inert gas environments to avoid tarnishing of silver. Our inkjet printed substrates can be developed on-demand, at the site of interest, to form silver nanostructures. Thus, our process eliminates the need to seal SERS substrates in inert gas environments and also vastly reduces the cost of production by eliminating the complex formulation steps required to prepare nanoparticle inks.

The ability to prepare ultra-low platinum loading electrodes for PEMFC applications using an additive, roll-to-roll compatible process, will be a significant impetus for enabling widespread automotive applications. Although, a few groups have reported the use of inkjet printers to fabricate MEAs using inks formulated from ionomer containing slurries of Pt/C particles, our proposed methodology will eliminate the need for colloidal ink formulation and can also enhance platinum utilization while lowering platinum loading by forming overlayers onto inkjet printed conductive, nanoporous thin film substrates.

## 3. Work Plan:

### 3.1 Methodology:

1. *Fabrication of SERS substrates*

The print-expose-develop process developed in our group will be used to fabricate SERS-active silver nanostructures with particle or nanowire morphology. These will then be used directly as SERS substrates or coated with gold, using standard photographic 'toning' process, to shift the plasmon resonance to longer wavelengths.

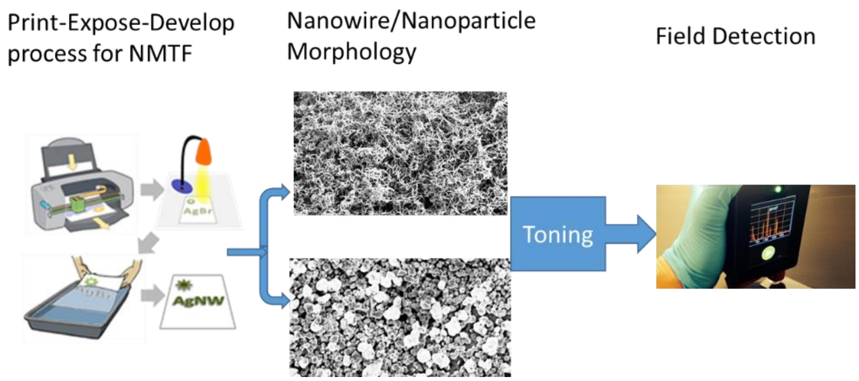


Fig.1 *Schematic illustrating the process flow for NMTF based SERS sensing.*

2. *Product development experiments*

We have already shown a proof-of-principle ability to detect pesticides on an apple, even well below MRL values, by swabbing using a paper-based SERS substrate. In this proposal, we want to further develop a field-deployable product, i.e. a robust SERS substrate that can be used to detect various classes of pesticides from vegetables/fruits procured in the marketplace. We envisage the following experiments to be undertaken:-

i. optimizing the "toning" process -- to produce gold coated silver nanostructures that have high enhancements using 785 nm laser source. This is deemed important as most handheld Raman analysers operate with 785 nm source, as these NIR lasers are better suited for miniaturisation.
ii. effect of nanostructure morphology – Comparison of the SERS performance of NMTF films comprising of wires vs. particles by adjusting the halide composition used in the printing process. For these optimization experiments, standard Raman probe molecules will be used.
iii. Pesticide molecule signatures -- pesticides corresponding to various chemical classes, viz. organophosphorus, organochlorines, carbamates and pyrethroids, will be tested by drop-casting to determine the level of detection using a confocal Raman microscope. These will be followed by trials using common formulations of these pesticide classes and also their combinations to identify appropriate signatures for field-identification of pesticides.
iv. Identification of 'best' paper/flexible substrate for swabbing – We have already identified kimwipes as the best cellulose-based substrate for printing SERS substrates. For field-based trials, we want to include a wider range of substrates, namely industrial

cleaning wipes and test them as possibly 'more-robust' substrates for swabbing. In these trials, produce from local markets will be spiked with known amounts of pesticides to estimate the swabbing efficiency of the different substrates.

v. Standard solvents or solvent mixtures (e.g. QUECHERS type) will be tested to determine their efficacy in picking up pesticide residues from fruit/vegetable surfaces.

3. *Spectral signature identification*

i. We have undertaken identification of component signatures in spectra using chemometric techniques earlier(Sivaraman et al.), and we expect the need to use similar techniques(Weng et al., 2015) for multi-component identification.

ii. Commercial pesticide formulations have several components and these can cause significant interference with the identification of the active pesticide component in the matrix. Under such circumstances, it will be prudent to optimize protocols for chromatographic separation using the paper substrate as the medium. For this channels with appropriate hydrophobic/hydrophilic nature will be patterned on the paper substrate using a wax-printer. Identification of appropriate solvent mixtures that lead to efficient separation of various classes of pesticides form their formulation matrix will also be carried out.

4. *Field trials of SERS substrates*

i. Produce from local markets (hopcoms), street vendors, supermarket chains, and Organic stores will be procured and tested for their pesticide content using portable Raman analyzer. These results will also be corraborated using the confocal Raman setup.

ii. The use of the SERS substrates with the portable Raman analyzer will be evaluated in the field/stores. Typically, about 20% of fruits/vegetables have detectable pesticide residues and 2% of produce have pesticides above MRL while 10% of 'organic' produce have detectable levels of pesticides, as determined using chromatographic techniques (FSSAI project report on 'Monitoring of Pesticide Residues at National Level', 2015).

5. *Printed NMTF as ORR catalyst*

i. We will use a self-terminating electrochemical deposition technique(Liu et al., 2012, 2015) to fabricate platinum overlayers, in steps of monoatomic shells, on printed silver nanowire networks. Electrochemical characterization of durability, stability and ORR activity will be carried out.

ii. We will also explore the use of nickel as the substrate for platinum overlayer coating, as platinum coated nickel catalysts exhibit excellent activity and are also inherently safe in terms of avoiding cations leaching and damaging PEMFC membranes during fuel cell operation.

The methodology envisaged involves the optimization of various aspects that will be carried out concurrently by Research students, Project Assistants, Masters students and summer interns. As such, we expect to follow the time schedule presented in the next section.

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