Nanomaterials-Enabled Photonic and Chemiresistive Sensing of Chemicals and Biochemicals

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ABSTRACT

Nanomaterials can enable superior sensing performance due to special characteristics that affect the interactions with target analytes as well as signal generation processes. We illustrate the critical role of nanomaterials for improved chemical and biochemical sensing using examples from our work on chemiresistive and plasmonic devices; performance studies have been done on gas-phase and solution-phase samples, respectively. We also highlight the importance of fabricating the incorporated nanomaterials by methods that are reproducible and manufacturable.

Keywords: biomarker, chemical microsensor, chemiresistive sensor, nanomaterials, photonic sensor

1 INTRODUCTION

Contact events occurring between target species and surface sites on sensing materials initiate front-end interactions and subsequent transduction processes that can yield viable signals for target detection. By offering high surface-to-volume ratios, and specialized properties, nanomaterials can significantly amplify the sensing responses realized. In this report, which briefly summarizes our poster presentation for the conference, we illustrate such principles for nanomaterials that have been incorporated for photonic and electronic sensing devices. The materials described have been tailored for these two sensing modalities to attain: 1) plasmonic enhancement (for surface-enhanced Raman spectroscopy - SERS, and localized surface plasmon resonance - LSPR), and 2) beneficial sensitivity in the electrical transport characteristics of chemiresistors, upon target molecule/species adsorption. The goal of our research is to enable tunable, high-performance chemical/biochemical sensing (in the gas phase and solution phase) on replaceable, low-cost sensing device platforms. We emphasize not only the benefits associated with fundamental nanoscale phenomena, but also the importance of employing newly developed methods to effectively incorporate the nanostructured materials with functional substrates.

2 RESULTS AND DISCUSSION

2.1 Nanodome Array Structures in Solution-Phase Sensing

Plasmonic enhancement factors for SERS of up to 10^8 have been produced using Ag nanodome arrays like that shown in Figure 1. The extremely high amplification that has been observed is directly associated with the small interdome gap spacing (≈ 15 nm), and our model calculations correlate closely with measured "hot spot" resonance characteristics [1]. High-resolution electron beam lithography is used to make a Si master template for the nanodomes, but a nanoreplica molding, roll-to-roll process can then be employed to inexpensively achieve precise array structures on disposable plastic coupons (Figure 2). Details of the lithographic steps for nanodome formation have been provided elsewhere [2]. The sensitive measurements made possible by the nanodome arrays offer opportunities for a range of analytical measurements, but our focus thus far has been directed towards biochemical applications connected to monitoring of drug levels (Figure 3) and biomarkers in bodily fluids.

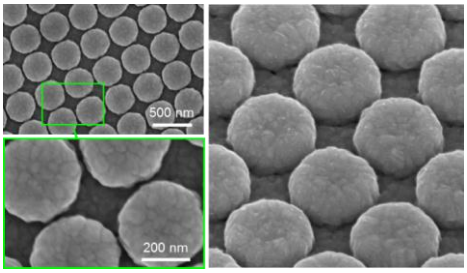

Figure 1. SEM images of a silver nanodome array substrate.

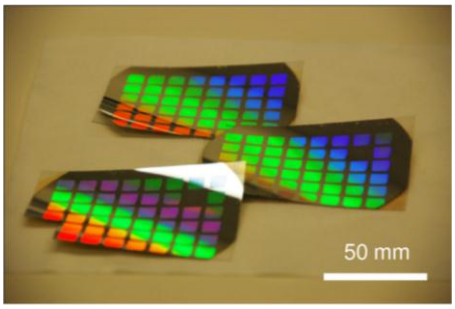

Figure 2. Image of nanodome array substrates fabricated on flexible plastic sheets, cut into (70 x 100) mm^2 areas.

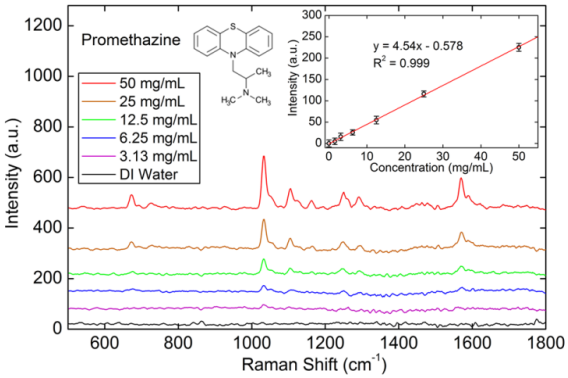

Figure 3. SERS spectra for promethazine solution measured using a nanodome array substrate. Inset: Raman intensity measured at 1030 cm^{-1} as a function of promethazine concentration.

2.2 Chemiresistive Nanomaterials in Gas-Phase Sensing

Nanostructured materials with a variety of compositions and morphologies have been coupled, as chemiresistors, with MEMS microhotplate arrays [3] (see Figure 4) to achieve gas-phase sensing devices that are application-tunable by choice of material type and temperature-modulation program. Prior work has focused on sensing films produced by self-lithographic CVD [4]; here we discuss micropipetting (and electrophoretic) techniques that allow a broad spectrum of preformed nanomaterials (see examples in Figure 5) to be locally deposited (and suitably fixed/annealed using the individual array microheaters). While the tunablity of the technology [5] allows trace level detection of many types of encountered target gases, for example, in process control, environmental monitoring and homeland security applications, we illustrate results for a biotechnological application connected to medical breath analysis [6]. Sensing elements with nanostructured materials demonstrated good sensitivity and selectivity for detection and quantification of multiple disease biomarkers in complex gas-phase mixtures (Figure 6).

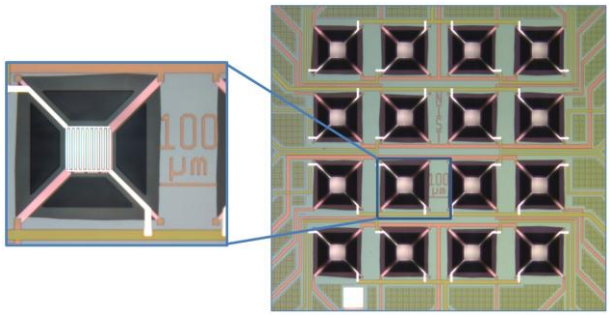

Figure 4. Micrograph of a single 100 µm MEMS microhotplate element (left), and 16-element array of such microhotplates, which are individually addressable (right).

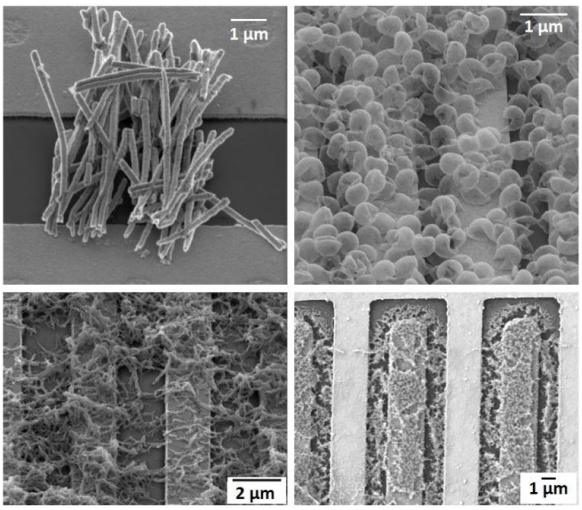

Figure 5. Examples of nanostructured materials incorporated into microhotplate arrays for chemiresistive sensing (CW from top left): tin nanowires, Sb:SnO_2 nanoparticle microshells, CuO sol gel and PANI fibers.

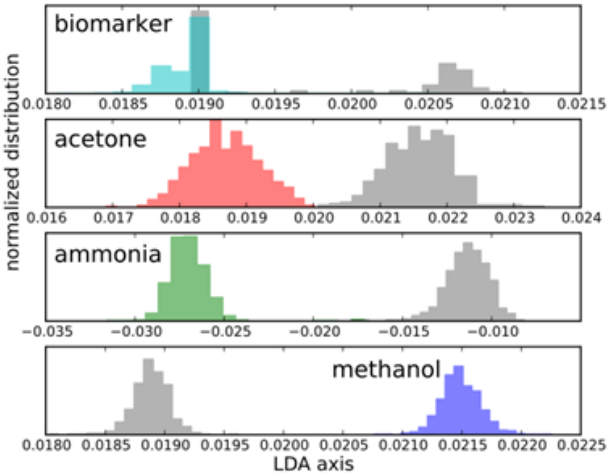

Figure 6. Separability of target-containing exposures from all other test exposures for several biomarkers (delivered at individual concentrations of 5 µmol/mol to 20 µmol/mol) in simulated breath.

3 CONCLUSION

Reliable sensing requires precisely-fabricated materials that provide stable interaction interfaces to the environment being probed. It is also desirable for the deposition methods used in forming the sensors to be both reproducible and facile in manufacturing, as these characteristics are required for successful commercialization. We have described the use of nanodome arrays for enhanced photonic sensing of target biochemicals, and the use of varied nanomaterials incorporated on MEMS microelements for chemiresistive sensing of gas-phase compounds. Example measurements

relate to monitoring of specific drug and biomarker concentrations, but both sensing approaches are versatile, and can be adapted for a range of sensing applications.

ACKNOWLEDGEMENTS

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