

# Novel Sensing Array Nanomaterials: Molecularly-Mediated Assemblies of Nanoparticles

Chuan-Jian Zhong <sup>a)\*</sup>, Susan Lu <sup>b)</sup>, Lingyan Wang <sup>a)</sup>, Xiajing Shi <sup>b)</sup>, Mark Schadt <sup>a)</sup>, Weibing Hao <sup>b)</sup>, Jin Luo <sup>a)</sup>

<sup>a)</sup> Department of Chemistry, & <sup>b)</sup> System and Industrial Engineering  
State University of New York at Binghamton, Binghamton, NY 13902.

\* To whom correspondence should be addressed (cjzhong@binghamton.edu)

## ABSTRACT

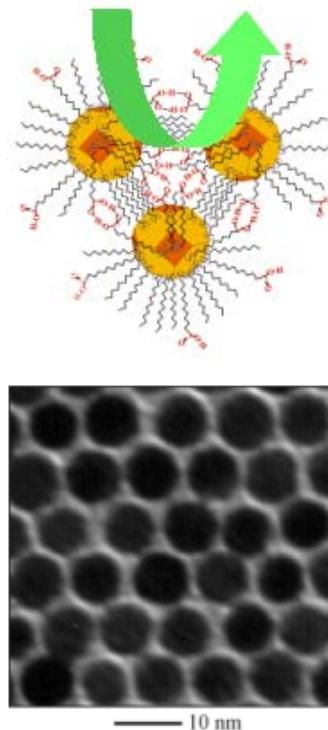
Nanostructured sensing arrays combined with pattern-recognition analysis are expected to provide new opportunities for enhancing the design of sensor materials in terms of sensitivity and selectivity. This paper describes an example in which the sensory properties of the thin film assemblies are exceptionally fine-tunable in terms of nanoparticle size, composition, thickness, and spatial properties. We discuss the results from an investigation of the design and construction of plug-and-play portable interdigitated microelectrode sensor arrays which involve a series of molecularly-mediated assemblies of nanoparticles on interdigitated microelectrodes for the detection of volatile organic compounds (VOCs) and the data analysis based on pattern recognition techniques. Our findings are significant because the nanostructure sequesters chemical or biological molecules into the interior or surface with porous access or specific binding properties, which alter or modify the electrical properties of the nanostructures.

**Keywords:** sensor arrays, nanoparticles, nanostructures, assemblies, volatile organic compounds

## 1 MOLECULARLY-MEDIATED THIN FILM ASSEMBLIES OF NANOPARTICLES

Nanostructured sensing arrays combined with pattern-recognition analysis are expected to provide new opportunities for enhancing the design of sensor materials in terms of sensitivity and selectivity [1]. The electronic and optical properties of the thin film assemblies are exceptionally fine-tunable in terms of nanoparticle size, composition, thickness, and spatial properties. Currently, some of the most extensively used techniques for thin film assemblies of nanoparticles include stepwise layer-by-layer assembly route, evaporation casting and polymeric matrix methods. Many of the approaches are labor-intensive, high cost, or lack of controllability over interfacial corruption during the multi-step assembly processes. The foundation of our approach is to couple molecular or polymeric mediation pathways to nanoparticles with pre-engineered shell structures. The understanding of how the sensory properties can be fine tuned by the size, composition and

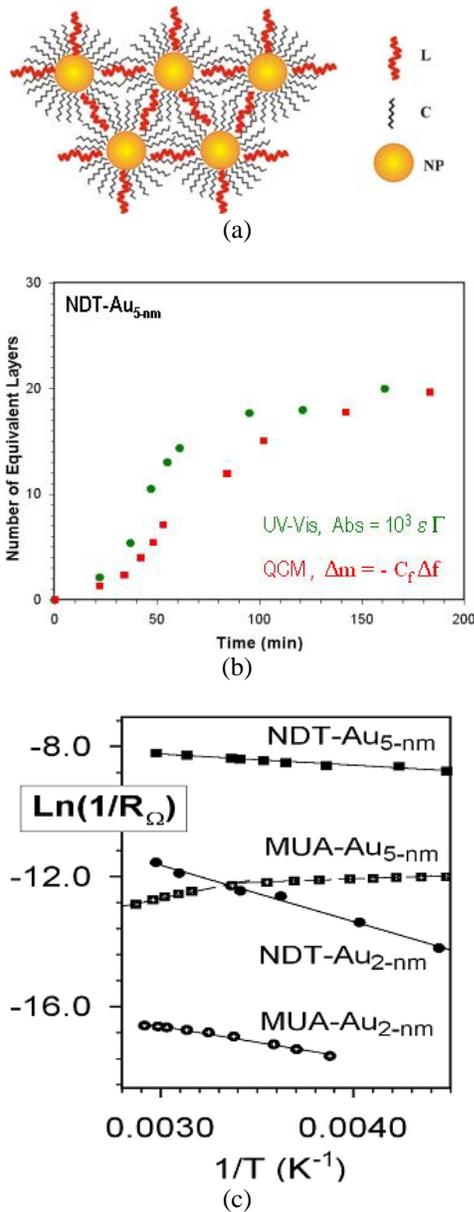
interparticle spatial properties of the molecularly-mediated assemblies of nanoparticles (Figure 1) is important to the development of novel sensing nanomaterials.



**Figure 1.** Hydrogen-bonding mediated thin film assembly of gold nanoparticles.

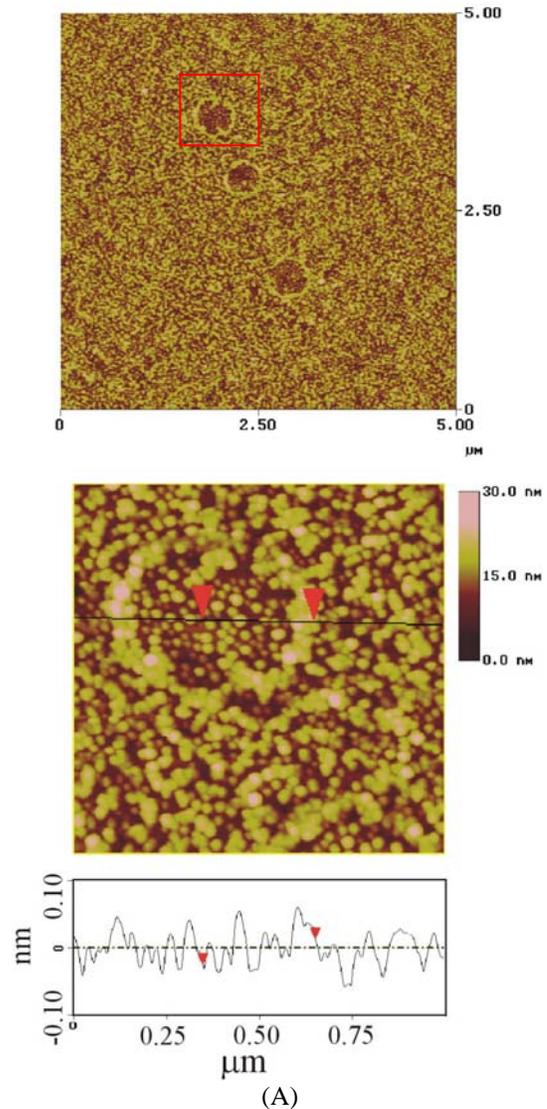
We recently developed a general mediation-templating route (Figure 2a) for assembling various metal nanoparticles with controllable interparticle spatial properties. The electronic conduction and optical properties of the thin films are fine-tunable in terms of size, composition, and spatial properties. For example, an initial exchange of free thiols with Au-bound thiolates (e.g., decanethiolate(DT)-capped Au) in solution followed by crosslinking of either inter-core Au-S bonding (e.g., nonanedithiol (NDT)) or inter-shell hydrogen-bonding agents (e.g., using 11-mercaptopundecanoic acid (MUA) or 15-mercaptohexadecanoic acid (MHA)) led to thin film formation with controllable ordering and thickness (Figures 3 and 4). In contrast to stepwise route, our one-step

assembly route is simple, and applicable to almost any substrate. Another example involved using a,ω-dicarboxylic acid functionalized molecular linkers (e.g., 1,6-hexanedicarboxylic acid (HAD)) to assemble AuAg alloy nanoparticles.

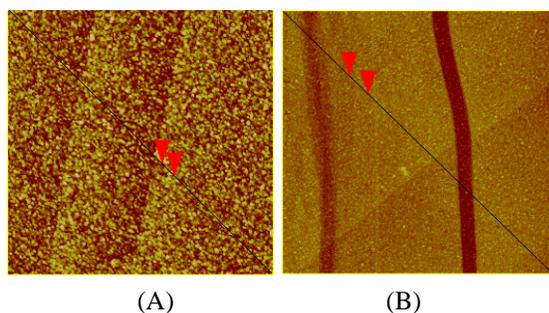


**Figure 2.** (a) Nanoparticle (NP) assembly linked by different linkers (L) and capping agents (C), and an example involving hydrogen-bonding (e.g., MHA linker) via carboxylic groups to link nanoparticles. (b) Thickness control of NDT-linked Nanoparticle assembly, (c) Plots of conductivity ( $\propto 1/R$ ) for Au nanoparticle thin film assemblies of different core sizes and linkers (NDT- & MUA-Au<sub>5-nm</sub> or Au<sub>2-nm</sub>).

The agreement between the thickness control as derived from the mass and the surface plasmon resonance band measurements (Figure 2b) demonstrates the nanoscale optical property being retained by the thin film assembly. The conductivity of these thin film assemblies was probed using interdigitated microelectrodes. Most of the films display thermally-activated conductivity property (Figure 2c), which demonstrates the fine-tunability of electronic properties in terms of size, composition, chain length, and functionality.



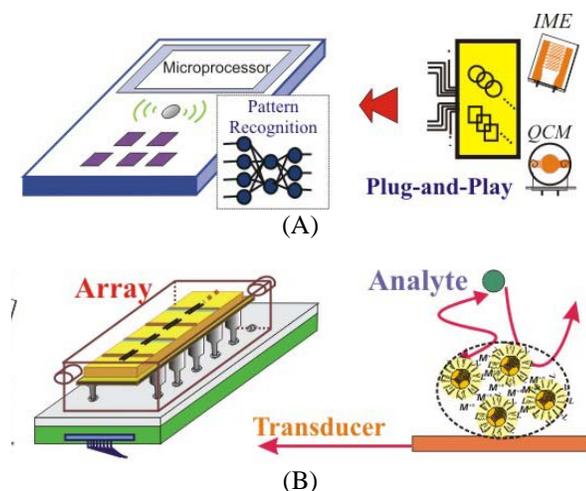
**Figure 3.** AFM images (5x5 μm<sup>2</sup>) of thin film assemblies of MUA-Au<sub>2-nm</sub> on annealed Au/mica (lower panel: a magnified image of the indicated area).



**Figure 4.** AFM images ( $5 \times 5 \mu\text{m}^2$ ) of thin film assemblies of (A) NDT-Au<sub>2-nm</sub> on HOPG, and (B) MUA-Au<sub>2-nm</sub> on HOPG.

## 2 SENSOR ARRAYS

We have been investigating the design and construction of plug-and-play portable sensor arrays including both hardware and nanostructured sensing array materials (Figure 5). The arrays involve the above nanostructured thin film materials for the detection of VOCs and the data analysis based on pattern recognition techniques.

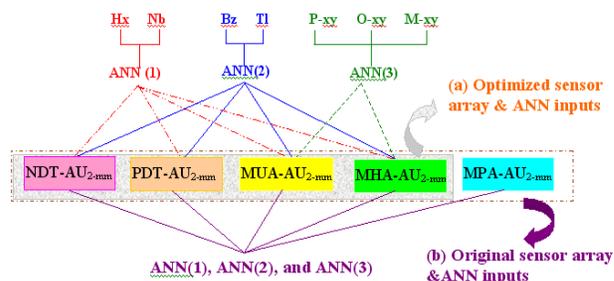


**Figure 5.** A schematic illustration of the plug-and-play portable sensor array system which involves interdigitated microelectrode (IME) and quartz-crystal microbalance (QCM) devices and pattern recognition techniques (A), and an illustration of an array of IME devices with nanostructured thin film materials for the detection of analytes (B).

The pattern recognition techniques involve principal component analysis (PCA) and artificial neural networks (ANN) techniques. The nanostructured array elements consist of thin film assemblies of alkanethiolate-monolayer-capped gold nanoparticles which were formed by molecularly-mediated assembly using mediators or linkers

of different chain lengths and functional groups. Each array element displayed linear responses to the vapor concentration. The observed high specificity to VOCs constitutes an unprecedented example resulting from the unique combination of hydrogen-bonding donor/acceptor and hydrophobicity in the interparticle structure. A set of ANNs along with PCAs was used for the analysis of a series of vapor responses. The PCA technique was used for feature extraction. A hierarchical BP neural networks system was employed as the pattern classifier, which was shown to enhance the correct pattern recognition rate. A satisfactory identification performance of the system has been demonstrated for a set of vapor responses. The results have also provided us important insights into the delineation of the design criteria for constructing nanostructured sensing arrays.

To further enhance the selectivity of the system array system, we recently developed a unique sensor array optimization technique, OMAC approach - Optimized Multi-module ANN Classifier. This method was developed to target sensor arrays for accurately detecting multiple VOCs [3c]. Each ANN module is dedicated to a subgroup/class of VOCs. More importantly, each ANN module has its own optimum inputs. In sensor array optimization, we attempted to identify the criteria and parameters for the selection of optimum combination of nanomaterials for a selected set of VOCs. Each sensor element's sensitivity and selectivity is quantitatively evaluated to assist the selection of sensing array materials, which also facilitates the selection of inputs to each dedicated neural network module. This OMAC method is shown to be useful for achieving a high overall recognition rate for a selected set of vapor analytes. We have used OMAC approach to recognize a set of seven VOCs using IME devices only. The optimum sensors for each group were first selected, and served as inputs to three corresponding neural network modules to perform classification (Figure 6, a).



**Figure 6.** Comparisons between optimized (a) and original sensor array & ANN inputs (b).

Table 1 shows a set of data for the recognition rate of classifiers with and without optimizing the sensing array in response to different VOCs.

Sensor array optimization	Hx	Bz	Tl	NB	p-Xyl	o-Xyl	m-Xyl
Yes	100%	100%	90%	100%	100%	100%	80%
No	90%	100%	90%	100%	40%	90%	40%

**Table 1.** Recognition rate of classifiers with and without optimizing the sensing array. Vapors: hexane (Hx), benzene (Bz), toluene (Tl), nitrobenzene (Nb), *p*-xylene (*p*-Xyl), *o*-xylene (*o*-Xyl), and *m*-xylene (*m*-Xyl).

Compared with non-optimized approach (Figure 6, b), it is observed that the classifier with optimized sensor array has significantly higher classification capability, including the smaller training data set size, reduced training time, and higher recognition rate, than the former one, especially for classification of xylenes. A 7-vapor test shows an average of 95% correct recognition rate.

## SUMMARY

The molecularly-mediated thin film assemblies of nanoparticles have been shown to exhibit fine-tunable sensory properties for the development of sensor array systems. We are currently refining our design parameters for building a prototype portable sensor array system for detecting VOCs and toxic or explosive gases. Another example for the nanostructured sensing involves thin film arrays on piezoelectric or microelectrodes transducers for the detection of chemical or biological species in air or water [2,3]. The understanding of this type of sensory properties and other nanostructured biomimetic or bioanalytical probes are also aided by pattern recognition [3] in terms of size, composition, interparticle distance and structure, dielectric medium, and interfacial affinity. Our findings are significant because the nanostructure sequesters chemical or biological molecules into the interior or surface with porous access or specific binding properties, which alter or modify the electrical or optical properties of the nanoscale materials.

## ACKNOWLEDGEMENT

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