High Recognition of Nanoparticles Stabilized by Different Structural Isomers through Matrix Imprinting [1]

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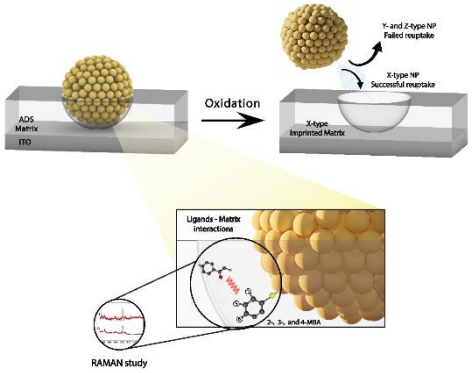
In the last years, nontoxicity has become at the forefront of research due to its relevance and importance to the environment and human health. Although the exposure risk to engineered nanomaterials depends on their physicochemical properties including their surface chemistry, the regulations are based mainly on the particle size. Since the use of NPs is unavoidable, there is an urgent need for small, easy-to-use, and field-available sensors for the detection of NPs. There is a wide range of laboratory techniques to characterize NPs spanning from electron microscopy to light scattering; however, most if not all of these are complex, cost-effective, and require skilled operators. Electrochemical detection methods would provide a cheap and easy tool to help characterize NPs based on their surface chemistry.

Recently, we introduced a different approach, termed nanoparticle-imprinted matrices (NAIM) that enables targeting the NP-matrix interactions [2]. In the NAIM approach, nanocavities with specific sizes, shapes, and chemical compositions are formed through the removal of imprinted NPs in thin matrices. These cavities are used to reuptake NPs very selectively based on their size, shape, and surface properties. The selectivity originates from both physical, i.e., size and shape of the NP, and chemical matching, i.e., proper interactions, between the NPs and the nanocavities. We have shown that such chemical and physical matching made it possible, on one hand, to differentiate between AuNPs of different sizes and, on the other hand, between NPs stabilized by different capping agents. Whereas the NAIM concept has resulted in an incredible selectivity, which is partially due to NP-matrix interactions, it does not disclose the physicochemical nature of these interactions that should be investigated by spectroscopy.

Here, we describe a NAIM-Raman combined study where we examined the imprinting and recognition of AuNPs stabilized by the three isomers of mercaptobenzoic acid (MBA) in an aryldiazonium electropolymerized based matrix. Specifically, identical 10 nm diameter AuNPs stabilized by the 2, 3, and 4-MBA isomers were formed by a ligand exchange reaction. Their adsorption on an indium tin oxide (ITO) surface modified by a positively charged polymer, e.g., polyethylenimine (PEI), was followed by the controlled electrografting of a thin 4-carboxyphenyl diazonium (ADS-COOH) film. The AuNPs were electrochemically dissolved and the reuptake of the different isomer stabilized AuNPs was studied by electrochemistry, Raman spectroscopy, and other techniques. We found a remarkable selectivity that must be attributed to chemical pairing, namely, to the specific interactions between the stabilizing isomer of the NP and the matrix. Specifically, the highest reuptake percentage was found for those NAIM systems that were imprinted and reuptaken with the same AuNPs isomer capping agent. In particular, the reuptake percentage of the originally imprinted AuNPs ranges from 60 to 80%, whereas the reuptake of AuNPs bearing different MBA isomer capping agents than those imprinted was substantially lower. The interactions between the MBA stabilizing the AuNPs and the aryldiazonium matrix were thoroughly studied by Raman spectroscopy and provided a molecular-level explanation for the performance of these NAIM systems.



1. High Recognition of Nanoparticles Stabilized by Different Structural Isomers through Matrix Imprinting. Din Zelikovich, Pavel Savchenko, and Daniel Mandler. **Submitted**
2. Shell–Matrix Interaction in Nanoparticle-Imprinted Matrices: Implications for Selective Nanoparticle Detection and Separation. **Din Zelikovich**, and Daniel Mandler. ***ACS Applied Nano Materials* 2021**