Molecularly imprinted polymers enhance detection capabilities

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A nanosensor based on molecularly imprinted polymers and surface-enhanced Raman scattering provides an effective and robust chemical sensing platform for detecting explosive targets.

The ‘global war on terror’ has made rapid detection and identification of energetic materials (substances capable of releasing large amounts of stored potential energy, such as propellants, fuels, and explosives) a priority for military and homeland defense applications. Detecting a diverse range of energetic materials that might be used in terrorist attacks, whether of ‘military grade’—e.g., 2,4,6-trinitrotoluene (TNT)—or ‘homemade’—e.g., triacetone triperoxide (TATP)—requires an adaptable sensor platform capable of rapidly recognizing a varied array of target chemical substances.

In particular, TNT is a commonly used explosive in the preparation of landmines for military and terrorist activities. Several methods for TNT detection have been reported, including fluorescent polymers, microcantilevers, ion mobility spectrometry, and Raman spectroscopy. Although such detection methods have been successfully employed, the current capabilities have some limitations. Those methods may not always be specific or extendable to other energetic materials of interest, and are not capable of detecting analytes in both the aqueous and gaseous states. Therefore, to improve on the current technologies and address present-day requirements for nanosensors (i.e., sensors that can detect very small particles or quantities of material), we are investigating a new sensing concept that integrates molecularly imprinted polymers (MIPs) and surface-enhanced Raman scattering (SERS) to enable enhanced detection: see Figure 1.

Molecular imprinting involves arranging polymerizable functional monomers around a template or target molecule, followed by polymerization and template removal. A schematic of a basic MIP fabrication strategy is illustrated in Figure 2. Arrangement is generally achieved by non-covalent or reversible covalent interactions. In both types of molecular imprinting, the template is removed, and 3D cavities are generated within the final material that are complementary to the template molecule in size, shape, and functionality. This allows preparation of polymers which act as artificial recognition elements that are selective for the adsorption of the target molecule of interest. We thus create a molecular ‘memory’ within the imprinted polymer matrix. The advantages of this technique include robustness and stability under a wide range of chemical conditions, and the ability to easily design recognition sites for a plethora of target chemicals (e.g., pesticides, energetic materials, pharmaceuticals, and proteins).

However, in chemical sensing applications, MIPs on their own do not meet the requirements for a sensor without some form of transducer to convert the analyte interaction into a measurable signal. A variety of electrochemical and optical transduction techniques applied to convert MIPs into sensors have been reported in the literature. In our work, we have examined the use of SERS—a spectroscopic technique

Figure 1. A highly selective sensing approach is achieved by integrating molecularly imprinted polymers (MIPs) for improved analyte selectivity and surface-enhanced Raman scattering (SERS) for analyte detection.
based on molecular vibrations—as a transduction method to achieve a high level of selectivity. This is an extremely sensitive and selective technique that involves enhancements in the Raman scattering intensities of analytes adsorbed on a roughened metal surface (typically, gold or silver). SERS provides vibrational spectra with unique chemical and structural information for a given species. The detection capabilities of SERS make it an excellent transduction method for selective and full compound identification, a capability that is not currently possible with existing MIP sensors.

That said, it should be noted that SERS-based techniques on their own have not typically proven to be useful for explosives detection. As any chemical components that enter the enhancing field can potentially contribute to the resulting spectra, making real-world samples difficult to differentiate. Thus, an integrated MIP and SERS concept is attractive because the MIP will concentrate the target to the SERS-active surface, making the combined approach more highly selective than a SERS-only detection scheme, and free from errors related to background interference.

To pursue this idea, we investigated a MIP-SERS sensing concept for the detection of TNT using a non-covalent imprinting approach. Polymerizable monomers were chosen based on potential non-covalent interactions with the TNT molecules, allowing for increased target recognition. The polymer matrix included a monomer with an amino group, which has been shown to engage in strong non-covalent interactions with TNT molecules, and therefore significantly improves polymer selectivity and affinity for TNT. We also considered adhesion of the MIP to the SERS-active surface (i.e., SERS substrate), and additional polymer precursors were chosen based on potential interactions with the metallic underlayer of the substrate. A monomer with a thiol group was also included in the polymer matrix and resulted in chemisorption of the polymer to the metal surface of the SERS substrate.

This integrated MIP-SERS sensor exhibited a 3 μM detection limit for TNT in solution. The response to the target analyte was reversible, and the sensor was stable in a variety of environments for at least 6 months. The MIP had preferential binding affinity for TNT compared to other structurally similar molecules. These results suggest that the MIP-SERS combination is an effective and robust chemical nanosensing scheme that could be extended to include other explosives of interest.

The hybrid MIP and SERS sensing concept shows promise in meeting and exceeding the requirements for a nanosensor. A successful MIP-SERS sensor platform could reduce sensor cost and size, while maintaining the high sensitivity, selectivity, and portability needed for military applications. We have also investigated other transduction methods using this non-covalent imprinting approach for TNT. Our next steps will include polymer optimization for improved template removal and analyte sensitivity, as well as investigating MIPs for other energetic materials, chemical warfare agents, and biomolecules.

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Ellen Holthoff is a research chemist at ARL. Her experimental work includes the development of microelectromechanical systems (MEMS)-scale photoacoustic sensor platforms for gas detection, molecularly imprinted polymers for chemical and biological sensing applications, and drop-on-demand inkjet printing for sample standardization.
References


