

# Silver nanoplates on graphite substrates for ultrasensitive and label free Surface-Enhanced Raman Scattering (SERS) based detection of organophosphorous nerve agents in gas phase

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## Abstract

A surface-enhanced Raman scattering (SERS)-based sensor has been developed for the label-free real-time gas phase detection of dimethyl methylphosphonate (DMMP); a surrogate molecule of the G-series nerve agents which are of particular concern due to its extreme toxicity, persistence and previous deployment. In particular, SERS substrates based on high density Ag nanoplates (LSPR at 700 nm) monolayers on graphite have been straightforwardly attained by electrostatically-driven adsorption technique. Unlike Au based counterparts, SERS measurements suggest the chemisorption of DMMP molecules to the Ag nanoplate surface, eventually leading to photoinduced decomposition products. These SERS substrates have demonstrated the capability for the reliable identification of DMMP in gas phase at 2.5 ppmV, with the advantages of simple operation and low cost.

**Key words:** SERS, neurotoxic agents identification, gas phase, real time detection, sub-ppmV

## Introduction

The G-series nerve agents, i.e. Tabun (GA), Sarin (GB), Soman (GD), are widely recognized as one of the most toxic group of chemical warfare agents (CWA) due to the presence of organophosphorus esters causing systemic effects predominantly on the central nervous system. Nowadays, the competing technologies for the rapid detection of chemical agents in gas phase face severe limitations in terms of specificity, portability, cost and simplicity.

SERS is one of the leading techniques for label-free ultrasensitive vibrational fingerprinting of a variety of molecular compounds [1]. In the field of explosives and chemical threat detection [2-3], SERS has been identified as key technology thanks to distinctive features such as: ultrahigh sensitivity, detection from a wide variety of matrices and quantification of multiple species in a single measurement, allowing real time detection in the field.

SERS detection at trace concentration levels in gas phase is hampered by the fact that only a

few molecules of interest are localized in very close vicinity (typically less than 10 nm) of the metal when localized surface plasmon nodes are excited. Many strategies address this problem, including the use of partition layers with low affinity and rapidly reversible binding sites [4-5] or the formation of stable complexes on the plasmonic surface [6]. In this work, real time SERS identification of DMMP has been demonstrated with Ag nanotriangle monolayers on graphite at 2.5 ppmV concentration. Their sensing performance has been assessed by comparison with Au based SERS substrates, already developed in our group [4].

## Preparation and Characterization of SERS substrates

The citrate capped Ag nanotriangles were synthesized according to published recipe [8]. The average edge length of Ag nanoplates is 38 nm (see Fig. 1) with the LSPR centred at 700 nm. The Ag assembly process was performed on graphite substrates previously coated with PDDA according to our previous works [4-5]. Graphite provides both

fluorescence quenching and surface area for nanoparticle dispersion.

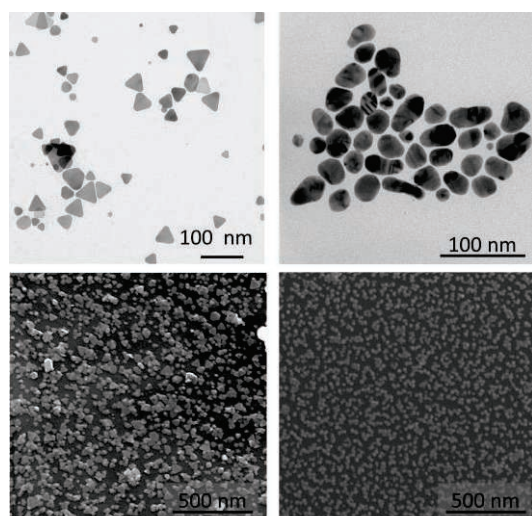


Fig. 1. TEM images of Ag (left) and Au (right) nanostructures (upper part), and SEM analysis of their assembled monolayers on graphite and SiO<sub>2</sub>/Si respectively (bottom part).

Raman experiments were conducted using Alpha 300 Raman spectrometer (WITec) with excitation wavelength of 785 nm and optical lens  $\times 50$ . R6G was chosen as probe molecule and the calculated EF and SERS gain (refer to [5] for details on calculations) are presented in Tab. 1. The EF and SERS gain values from Au assemblies were circa one order of magnitude weaker than that from Ag, in agreement with the electromagnetic theory. However, the superior SERS performance of Ag is hampered by its poor stability, i.e. EF and SERS gain decays almost one order of magnitude on samples exposed to room conditions (aged) for 2 months. Our efforts are devoted to on-demand assembly of active SERS substrates directly prior to experiment to minimize potential ambient degradation of the Ag surfaces.

Tab. 1: Enhancement factor and SERS gain for the Ag and Au based substrates studied in this work.

	Ag_Graphite (fresh)	Ag_Graphite (aged)	Au_SiO <sub>2</sub> /Si
EF	$5.31 \times 10^5$	$7.79 \times 10^4$	$7.21 \times 10^4$
Gain	$1.33 \times 10^8$	$2.53 \times 10^7$	$1.80 \times 10^7$

### SERS Detection in Gas Phase of DMMP

A nitrogen stream containing 2.5 ppmV of DMMP was fed to the home-made exposure cell where the SERS substrate was mounted [4-5]. The characteristic Raman signature of DMMP, with main bands at 515, 710 and 814 cm<sup>-1</sup>, are clearly developed upon 15 min exposure on Ag substrates (see Fig. 2). The

limit of detection of DMMP could be down to 725 ppb. Opposed to Au substrates, the Raman bands of citrate species are attenuated, and the photo degradation of the target analyte is diminished thanks to graphite. Analyzing the time-dependent evolution of SERS spectra, chemisorption of DMMP molecules and subsequent decomposition reaction on Ag surface is postulated. Further efforts are focused on DFT calculations to get insight the formation of Ag-DMMP complexes.

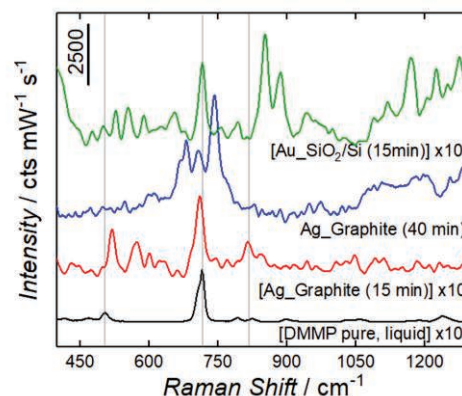


Fig. 2. SERS spectra of high-density Au and Ag monolayers during exposure to 2.5 ppmV DMMP.

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