

Hand-Held Femtogram Detection of Hazardous Picric Acid with Hydrophobic Ag Nanopillar SERS Substrates and Mechanism of Elasto-Capillarity

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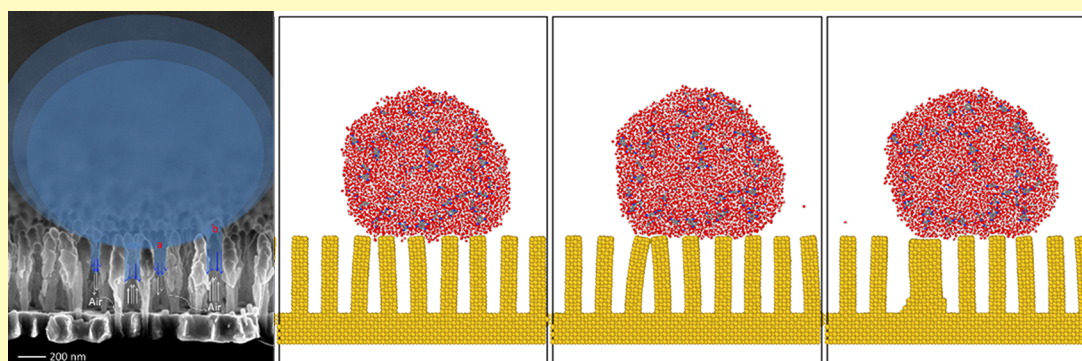
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Supporting Information



ABSTRACT: Picric acid (PA) is a severe environmental and security risk due to its unstable, toxic, and explosive properties. It is also challenging to detect in trace amounts and in situ because of its highly acidic and anionic character. Here, we assess sensing of PA under nonlaboratory conditions using surface-enhanced Raman scattering (SERS) silver nanopillar substrates and hand-held Raman spectroscopy equipment. The advancing elasto-capillarity effects are explained by molecular dynamics simulations. We obtain a SERS PA detection limit on the order of 20 ppt, corresponding attomole amounts, which together with the simple analysis methodology demonstrates that the presented approach is highly competitive for ultrasensitive analysis in the field.

KEYWORDS: SERS, picric acid, elasto-capillarity, hydrophobic Ag nanopillars, flexible hot-spots, molecular dynamics simulations

Picric acid (PA) or 2,4,6-trinitrophenol (TNP) is an old and well-known high explosive, but mounting security concerns has led to a renewed interest and an outburst of publications.¹ PA is highly unstable, in addition to being toxic and cancerous and, therefore, a serious security liability.^{1a–v} There is an urgent need for highly sensitive PA sensors for water samples since large amounts have been released from industrial use, leading to accumulation in rivers, lakes, and groundwater.^{1a–v} The marketing and use of some explosive

precursors have recently been regulated within the European Union (EU No 98/2013) to prevent illicit manufacture. However, some explosives, including PA, can still be synthesized from freely available chemicals. PA is a solid with low vapor pressure and a relatively high water solubility (12.7

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g/L), which makes it difficult to detect in vapor phase at ambient temperatures. PA present as dust is classified as a sensitizing substance and has recently been assigned a new low permissible exposure limit (0.1 mg/m^3 8 h TWA). To this end, robust, sensitive, and selective PA detection methods need to be developed, both to avert terrorist threats as well as for monitoring environmental pollution.¹

Most recent works on PA have dealt with the issue of trace detection and sensing, in particular based on fluorescence techniques.¹ Surface-enhanced Raman scattering (SERS) spectroscopy is widely recognized as an ultrasensitive method to detect, e.g., biomolecules² and explosives,³ and in particular conjugated nitro-explosives such as TNT and PA.^{3b} Despite this, the first SERS studies of PA appeared only recently.^{3e,4,5} For example, Stewart et al.⁵ demonstrated a detection limit of $20 \mu\text{M}$ PA on positively charged Ag nanoparticles and pointed out the difficulty of measuring anions, such as PA, on SERS active gold or silver due to the negative zeta potential of these metals. The lowest SERS detection limit for PA, $0.46 \mu\text{M}$ using a hybrid silver-magnetite detection scheme, was reported recently.⁴

We have recently reported that gold-on-silicon nanopillar SERS substrates exhibit extraordinary properties for detecting the nerve gases VX and Tabun.⁶ We here use similar substrates in which the Au has been replaced by silver. This type of substrate has been described previously⁷ and further optimized.⁸ Briefly, the samples consist of a Si-nanopillar base substrate, obtained through reactive ion etching, covered by 225 nm evaporated Ag. The resulting “nano-forest”⁹ of flexible Ag nanopillars, shown in Figure 1, turned out to be less

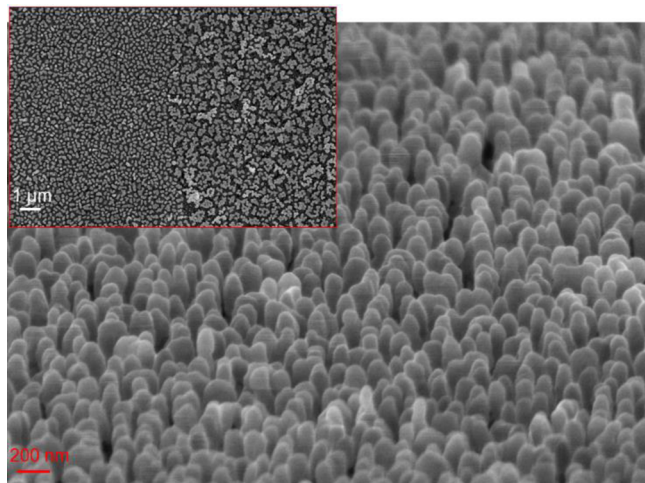


Figure 1. Tilted SEM image of the silver nanopillar SERS substrates used in this study. Inset shows the substrate at an evaporated droplet interface, where the droplet has generated clustering to the right.

hydrophobic than the gold substrates. Hence, it was easier to place and hold small water based droplets on them with good precision. The droplets almost immediately adhered, similar to the Au-nanopillar case, with high contact angles ($120\text{--}140^\circ$) characteristic of hydrophobic surfaces. If a droplet is placed on a substrate and left to evaporate, elasto-capillary forces pull the nanopillars together, resulting in SERS hot-spot clusters.⁶ This is illustrated by the SEM image inset in Figure 1, which shows the edge between a pristine surface region and a region where a droplet containing a low concentration of PA (0.4 ppb) has dried out. Similar hot-spot generating clustering has been

observed previously on several gold and silver substrates, e.g., in ref 10. The clustering effect also creates a macroscopically visible spot on the substrates (ca. 1.5 mm diameter from a $2 \mu\text{L}$ droplet). Such spots can be clearly seen on silver-based substrates under normal lighting conditions, whereas Au-substrates require very bright light. Figure 2 illustrates how

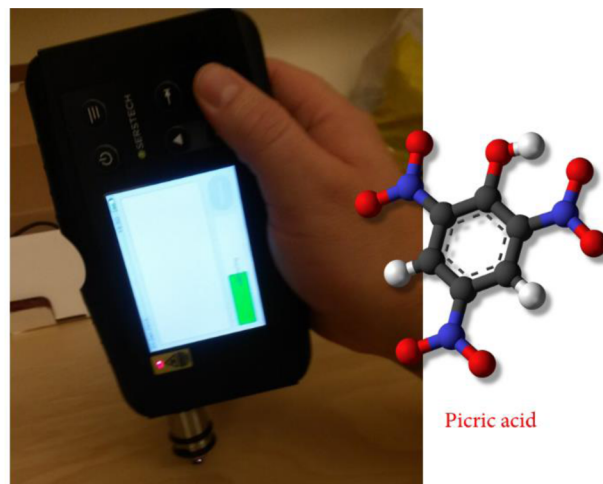


Figure 2. Raman instrument during hand-held measurement on a SERS substrate and a molecular model of picric acid.

we used a hand-held Raman instrument (Serstech 100 Indicator) to measure SERS from PA (molecular model in Figure 2 inset) on the Ag nanopillar substrates. Rapid droplet adhesion, clearly visible drying stains, and the possibility to perform hand-held measurements is clearly a powerful and convenient combination for SERS analysis in the field and outside dedicated laboratories.

The SERS spectrum in Figure 3a from an evaporated $2 \mu\text{L}$ droplet with 20 ppb PA in water shows several distinctive

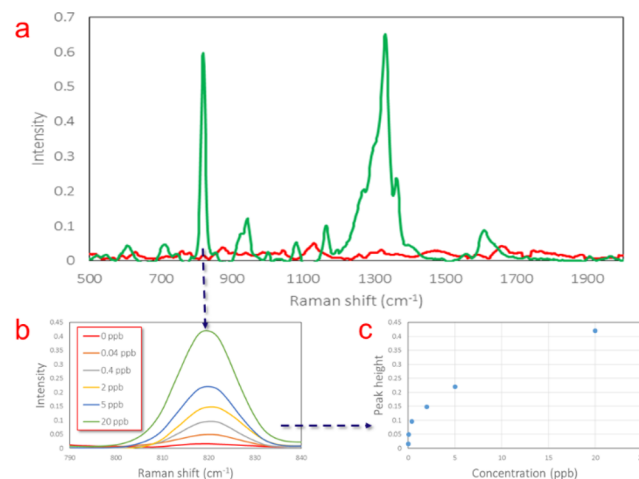


Figure 3. (a) Hand-held instrument Serstech SERS spectrum of picric acid ($2 \mu\text{L}$, 20 ppb) and background (red). (b) Concentration dependence of the 820 cm^{-1} peak. (c) PA calibration curve.

peaks, of which the major ones are at 820 and 1332 cm^{-1} and are both related to vibrational modes of the NO_2 -group.¹¹ In Table S1, all identified peaks are listed and compared with literature SERS and Raman studies,^{5,11a} and a high correlation is seen, especially with the SERS study. Figure 3b shows the

820 cm^{-1} peak at different concentrations of picric acid (0–20 ppb, averaged spectra, $n_{\text{Tot}} = 22$). The measurements were acquired as shown in Figure 2, with the following experimental parameters: 785 nm/165 mW laser, 2 s acquisition time, 50 μm^2 spotsize, and 0.3 numerical aperture of the outermost lens. A nice trend is seen in the calibration curve (Figure 3c), and as typically seen in SERS, a rapidly declining signal, which is common, is likely due to hot-spot saturation.¹² The lowest explicitly measured concentration was 0.04 ppb, and the 2 μL droplet equals to a total amount of 80 fg or 350 attomol. From zero level noise (σ) and the slope (k) to the 0.04 ppb level, the detection limit ($\text{LOD} = 3\sigma/k$)¹³ was calculated to be 18 ppt (parts per trillion; total amount 36 fg, 160 attomol), and limit of quantification (LOQ) was 0.06 ppb. For a brief comparison with the literature, the previously mentioned SERS study showed a LOD of 0.46 μM which equals about 110 ppb, i.e., approximately 3–4 orders of magnitude higher. Looking at other techniques, a very impressive LOD was demonstrated recently by Malik et al.,^{1m} 7 ppt or 31 pM, and the lowest explicitly detected PA concentration was 200 pM or 46 ppt, i.e., very similar results to those in the present study (18 and 40 ppt). The technique used by Malik et al. was fluorescence quenching based, which is by far the most used sensing method for picric acid. Additionally, for our most impressive results regarding totally loaded amounts of PA, comparative numbers are not present in the Malik et al. study. For a brief comparison with the in-laboratory gold standard for everything difficult to measure, mass-spectrometry, which quite commonly achieves detection limits in the femtogram range, however, with a quick overview of the literature, picogram detection of picric acid was the best to be found.¹⁴

Further insights into the nanofluidics of PA/water droplets on Ag nanopillar surfaces were investigated by molecular dynamics (MD) simulations.¹⁵ MD simulations were carried out to study the wetting and evaporation process on an Ag nanopillared surface, as shown in Figure 4. Each Ag nanopillar has a height of 4.09 nm and a width of 0.82 nm, and the Ag–Ag interactions are modeled by (EAM) potential.¹⁶ 5,000 water molecules and 100 PA molecules were mixed together using Packmol.¹⁷ The water TIP4P/2005 model was used,¹⁸ and PA was described by the Merck Molecular ForceField.¹⁹ The temperature of the system was maintained at 300 K using a Berendsen thermostat. A time step of 1.0 fs was used. All of the MD simulations were performed using LAMMPS.²⁰ We also calculated the surface tension of water and PA solution using the Kirkwood-Buff formula.²¹ Our MD results show that the surface tension for pure water and PA/water solution are 62.8 and 72.5 mN/m, respectively, i.e., the PA molecules increase the surface tension compared with that of pure water.

The droplet of PA solution, with a diameter of about 9.0 nm, was brought to connect with the pillared surface and then started to wet the surface. Because of the elasto-capillary interactions²² between the liquid and Ag, the Ag nanopillars show bending deformations, as shown in Figure 4 (green panel) and Movie S1. If two nanopillars are close enough, they collapse which results in the clustering, as shown in Figure 4. After that, the evaporation simulation was conducted, starting with the equilibrium state obtained in the simulations of the wetting process, and the evaporation evolved as shown in Figure 4 (blue panel) and Movie S2. The procedure for evaporation has been described in previous work.²³ Also shown in previous work is that the evaporation could lead to further bending of nanopillars,¹⁵ which may enhance the clustering of

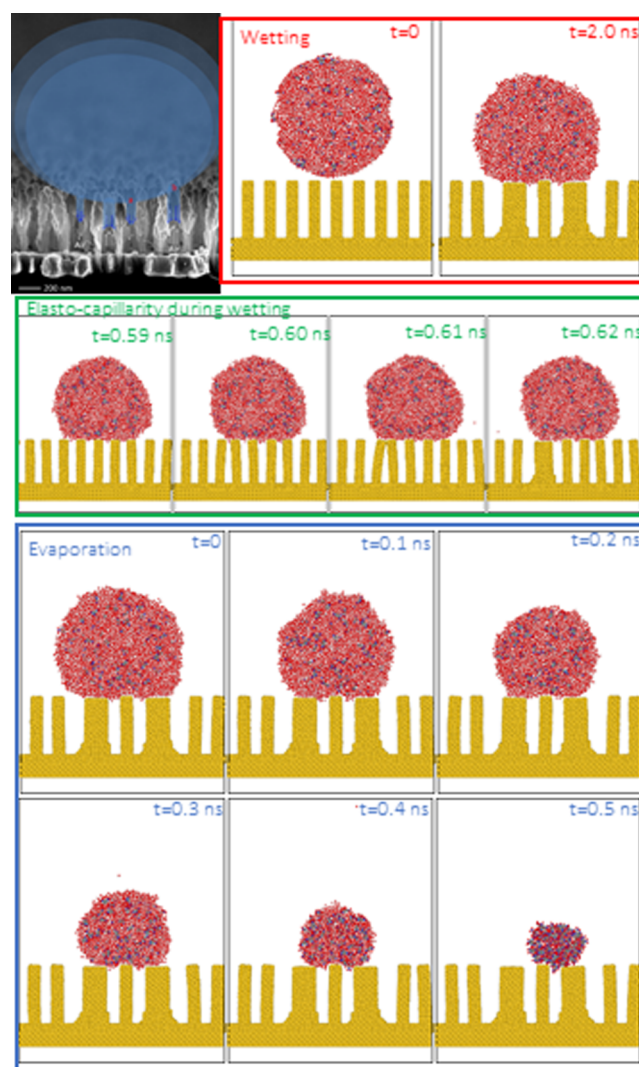


Figure 4. Top: profile SEM image of the Ag nanopillar substrates. Illustrated on top is an evaporating water droplet. Red panel: MD snapshots of the droplet of PA solution wetting on the Ag pillared surface. Balls with different colors were used to denote different types of atoms: oxygen (red); hydrogen (white); carbon (gray); nitrogen (blue); and Ag (yellow). Left, initial state; right, equilibrium state at 2.0 ns. Green panel: clustering of two Ag nanopillars due to the elasto-capillarity interactions. Blue panel: MD snapshots of evaporation of a droplet of PA solution on Ag nanopillars.

Ag nanopillars. However, we could not observe such results in this evaporation case. The reason may be that the clustering in the wetting process increases the bending stiffness of Ag nanopillars. Nevertheless, these MD simulation results demonstrate that the elasto-capillarity effect is crucial for the clustering of Ag pillars observed in experiments.

In conclusion, picric acid is an interesting molecule in many aspects affecting human sustainability and living on many levels. Its high acidity and negative charge in most natural environments present analytical challenges, especially for plasmonic based sensing with gold or silver substrates. We demonstrate the first example of ultrasensitive SERS of picric acid on bare silver substrates. Particular nanofluidics and plasmonics are beneficial, leading to the enrichment of PA molecules in SERS hot-spots. Experiments and molecular dynamics simulations show that elasto-capillarity is crucial for these signal accumulating effects. With a small and simple hand-held device,

sensitivity and detection are in level with or even better than state of the art techniques for picric acid today, including mass-spectrometry. Low femtogram detection is achieved from 2 μ L droplets of 40 ppt picric acid.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssens.6b00749.

Raman peaks (PDF)

MD simulation of the wetting (AVI)

MD simulation of the evaporation (AVI)

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Notes

The authors declare no competing financial interest.

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