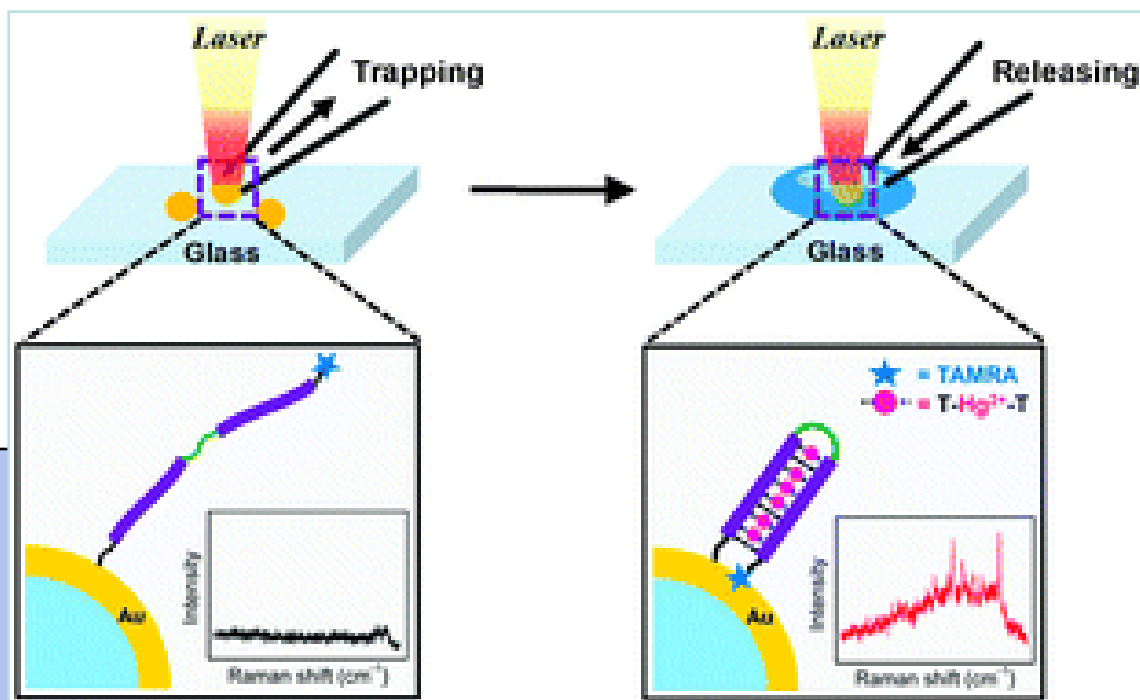


Mercury(II) detection by SERS based on a single gold microshell



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Introduction

Mercury → A highly toxic contaminant in aquatic ecosystems and pose severe risk to human health and the environment that exists in metallic, inorganic, and organic forms.

- Existing methods for sensing Hg^{2+} ion → Organic chromophores, fluorophores, conjugated polymers, electrochemical methods, quantum dots, nanoparticles (AuNPs), etc. based methods.
- Limitations → Insufficient selectivity, sensitivity and interference of other competing metals.

Surface-enhanced Raman scattering (SERS) → A powerful spectroscopy technique that can provide non-destructive and ultrasensitive characterization down to single molecular level.

Limitations

- Metals such as Ag, Au and Cu are required to either have roughened surfaces or be in the form of nanoparticles for a substantial SERS effect.
- Since the nanoparticles are invisible by conventional optical microscopy, it is difficult to place them on the point of interest and to ensure they are present.
- Individual nanoparticles are too small to be manipulated, and thus hard to remove from the surface after SERS measurements.

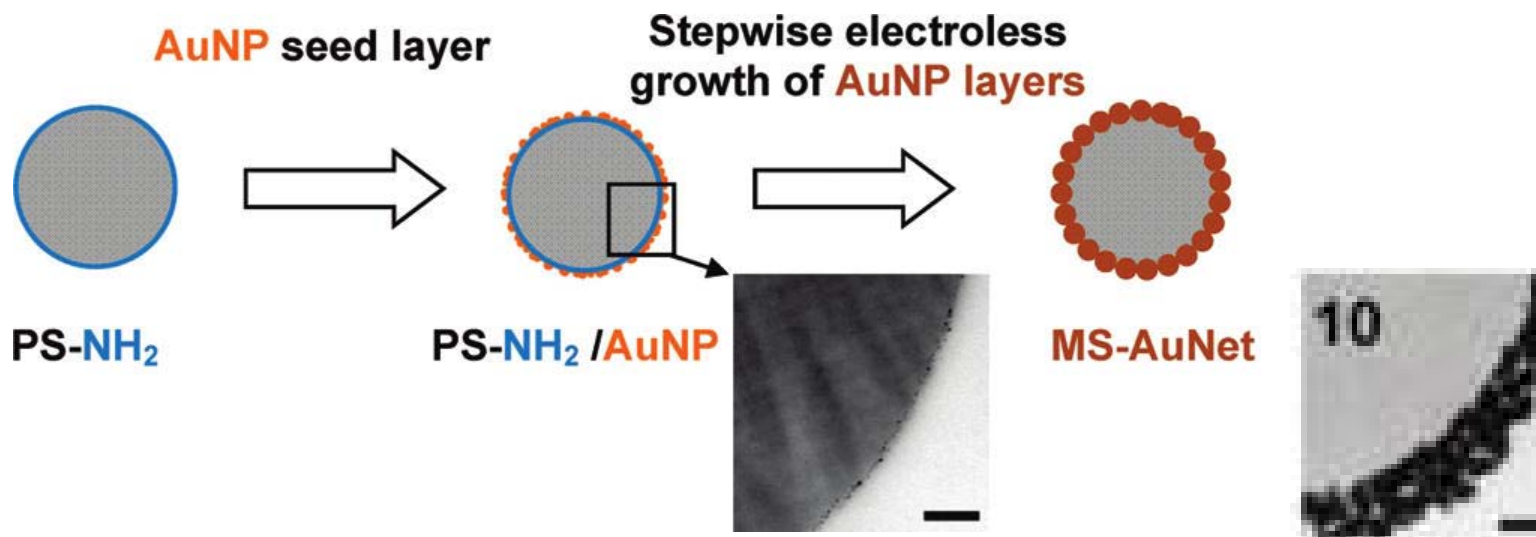
About the paper

A unique method for sensitive and selective detection of Hg^{2+} ions using DNA-modified gold microshells which can be individually manipulated using a micropipette and act as a micro SERS probe for analysis in small sample volumes.

- **SERS substrate used** → Highly SERS active gold microshells.
- **Sensing principle** → Conformational change of the nucleic acid strands that are immobilized on a gold microshell.
- **SERS probe molecule** → Doubly labeled DNA with thiol and tetramethylrhodamine (TAMRA) end groups.
- **Reaction** → Complexation of Thymine (T)-rich single-stranded DNA with Hg^{2+} and the formation of specific T- Hg^{2+} -T complex.

1. Preparation of gold microshells

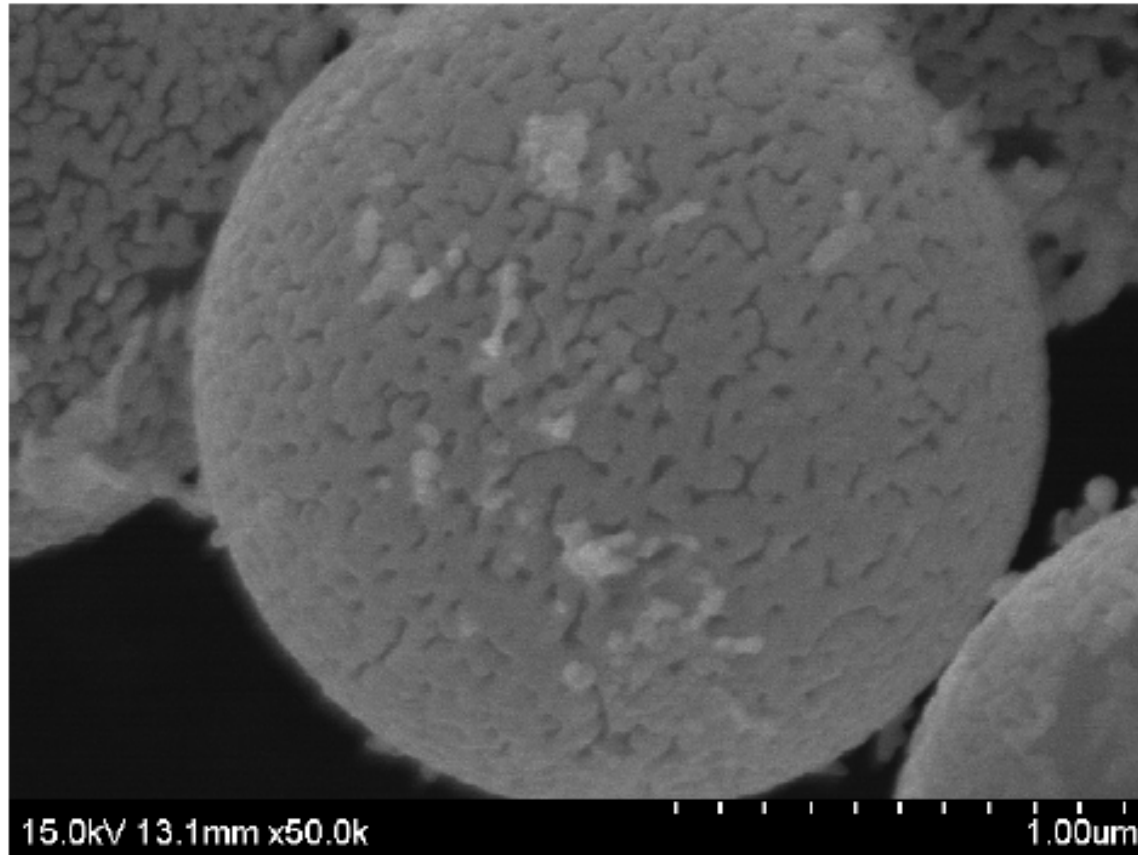
- Gold nanoparticle synthesis.
- Attachment of AuNP seed layers to amine-terminated polystyrene beads (PS-NH₂).
- Electroless Au plating using potassium carbonate (0.018 mmol) and 15 mL of 1% Au³⁺.



2. Functionalization of gold microshells with DNA

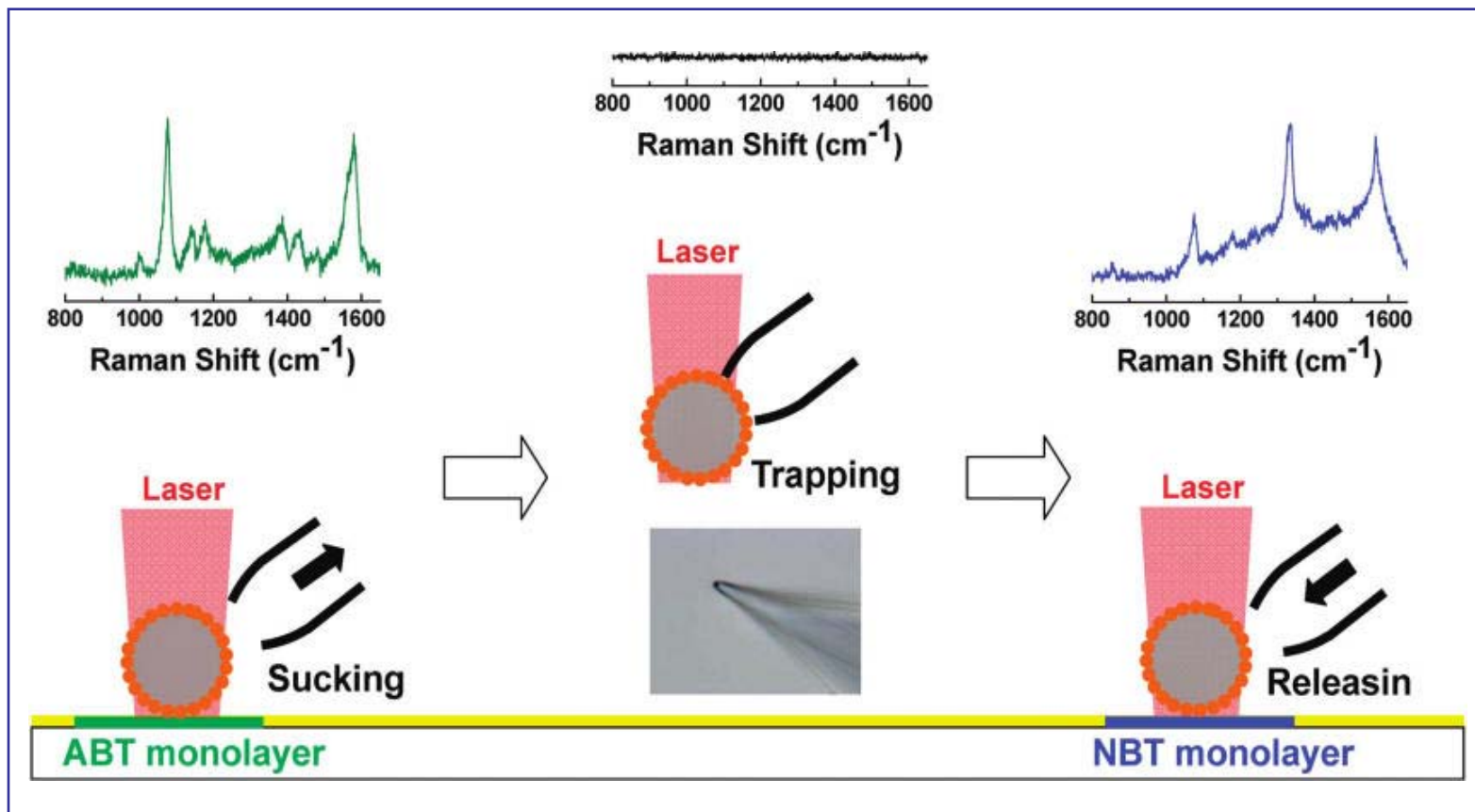
3. Trapping a DNA-modified single gold microshell at the tip of the micropipette and manipulation

Micropipettes were fabricated by heating and pulling borosilicate glass capillaries in a laser-based micropipette puller device.



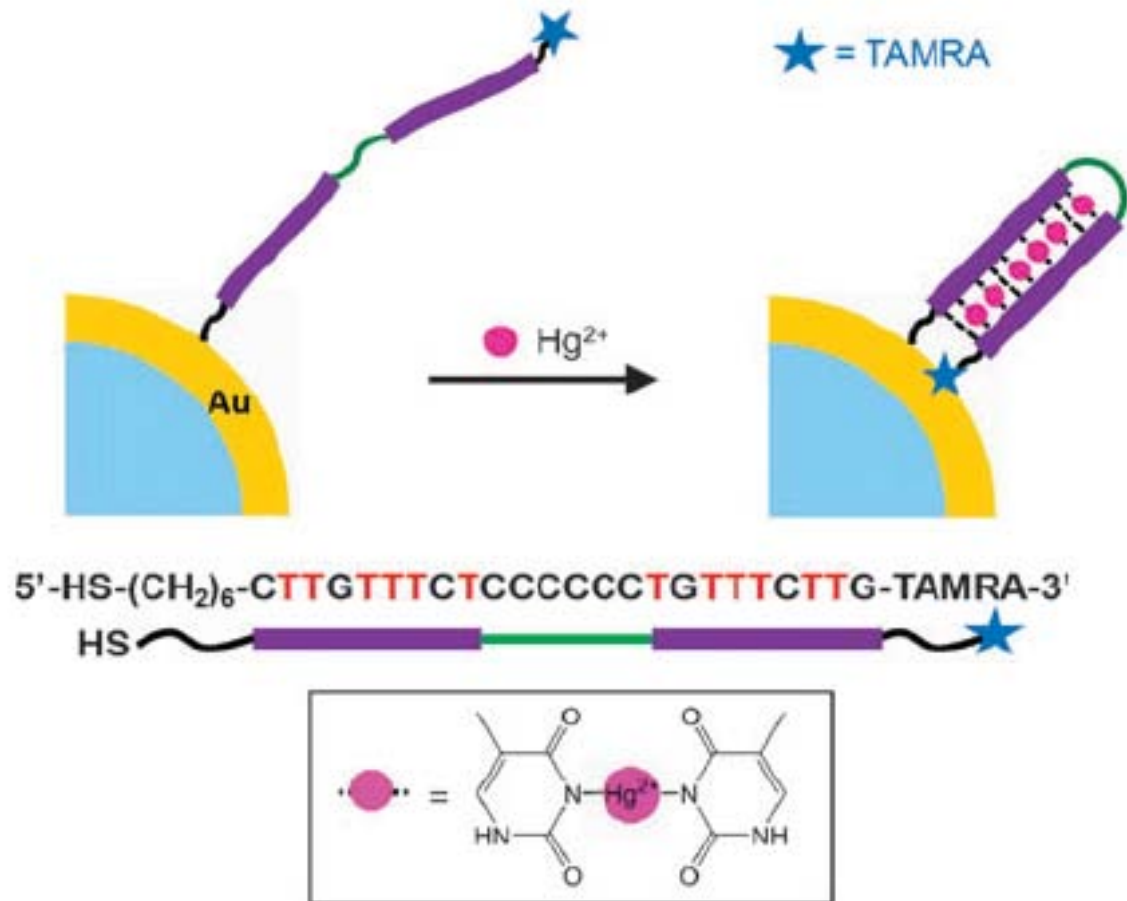
Scanning electron microscopy (SEM) image of gold microshells composed of (PS-NH₂/AuNPs) with the diameter of 2 μ m.

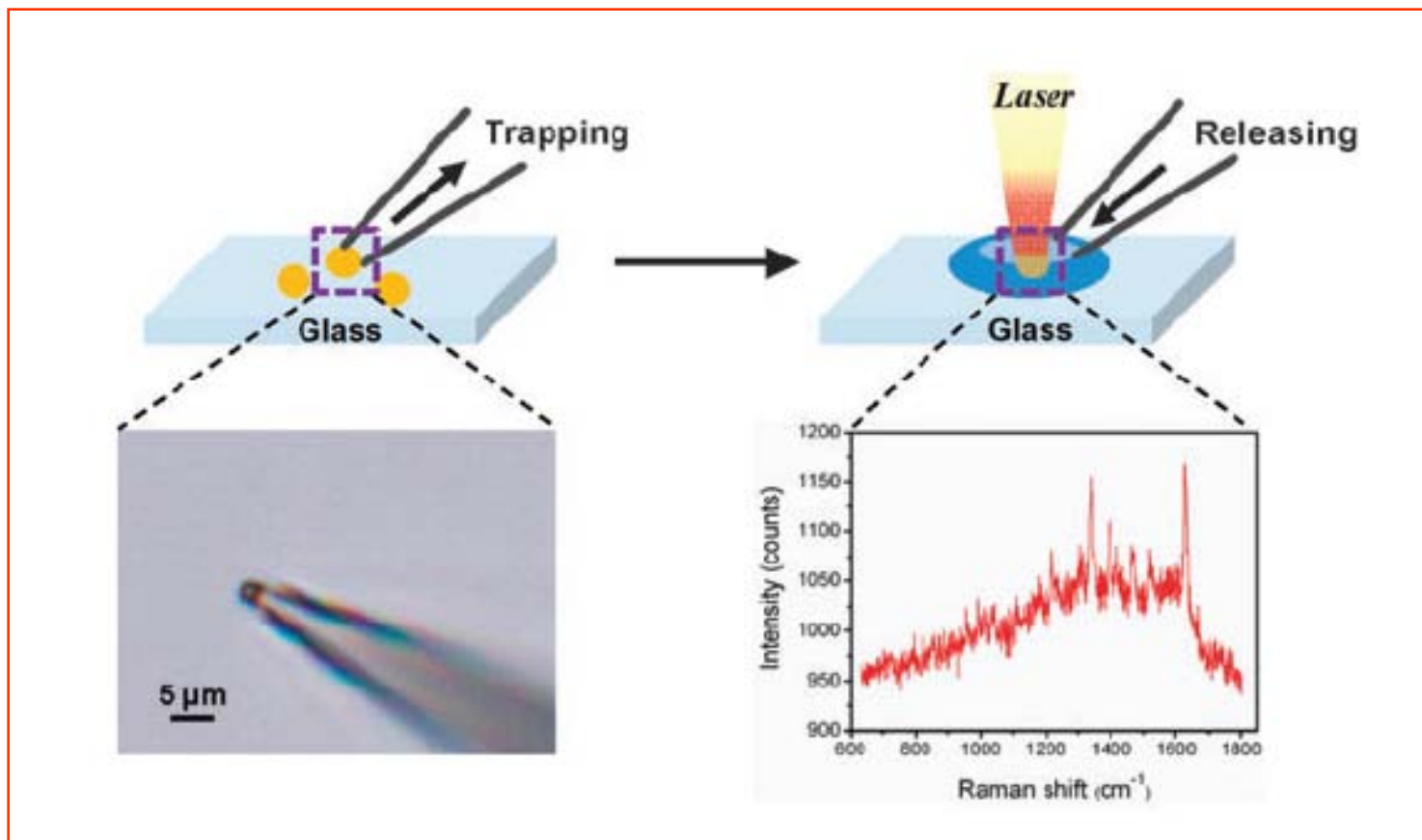
Verification of no contamination during surface identification



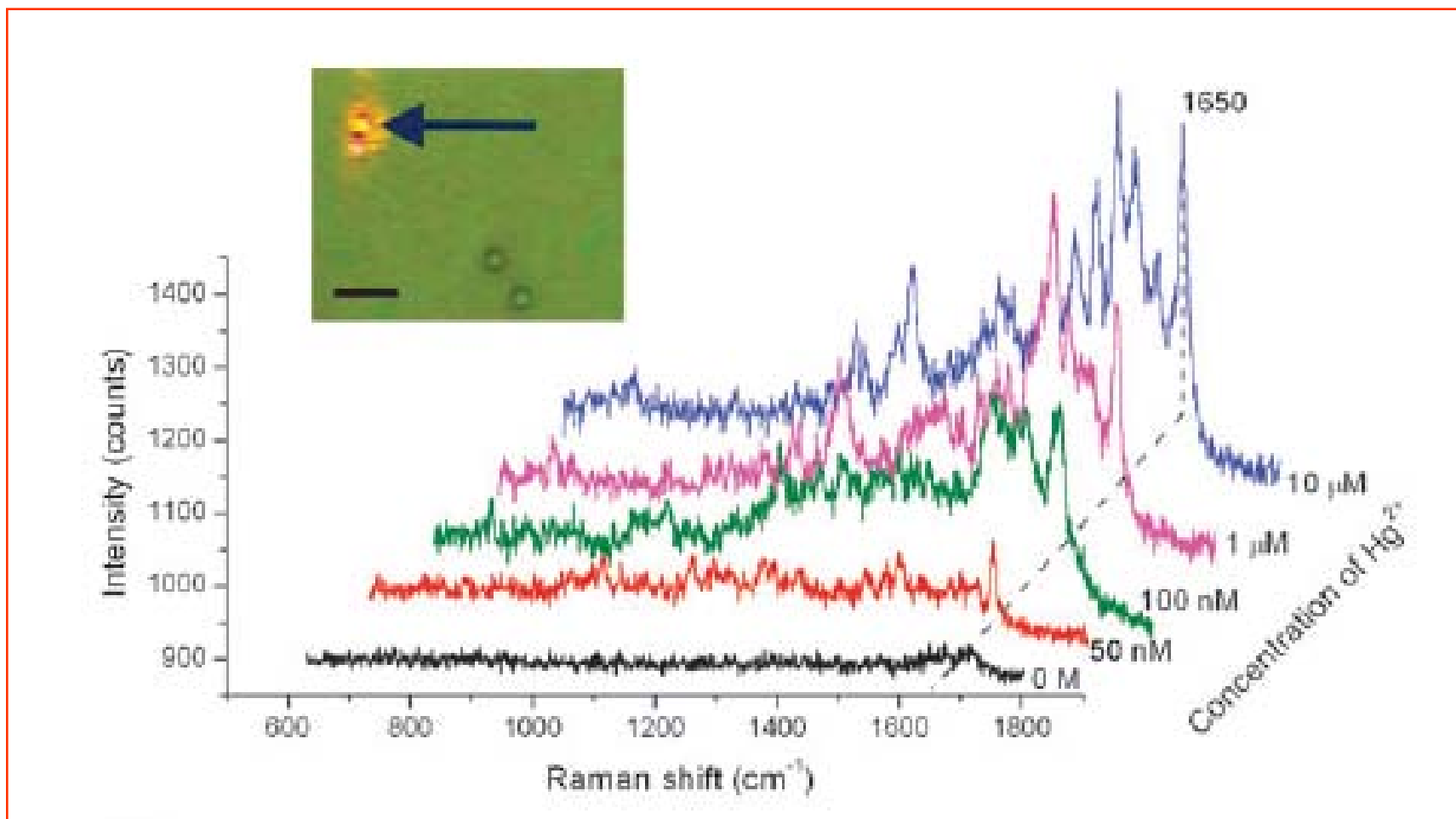
Scheme of transferring and placing a MS-AuNet on the spots of interest. SERS spectra were obtained from a bare MS-AuNet placed on the ABT layers (green), trapped at the tip end of a micropipet (black), and released on NBT monolayers on another spot (blue). Both organic monolayers are on Au substrates, and the SERS spectra are from one MS-AuNet carried by a micropipet. The acquisition time was 1 s. An optical microscope image shows a MS-AuNet trapped at the tip end of a micropipet.

Schematic description of the SERS sensor for Hg^{2+} ion detection



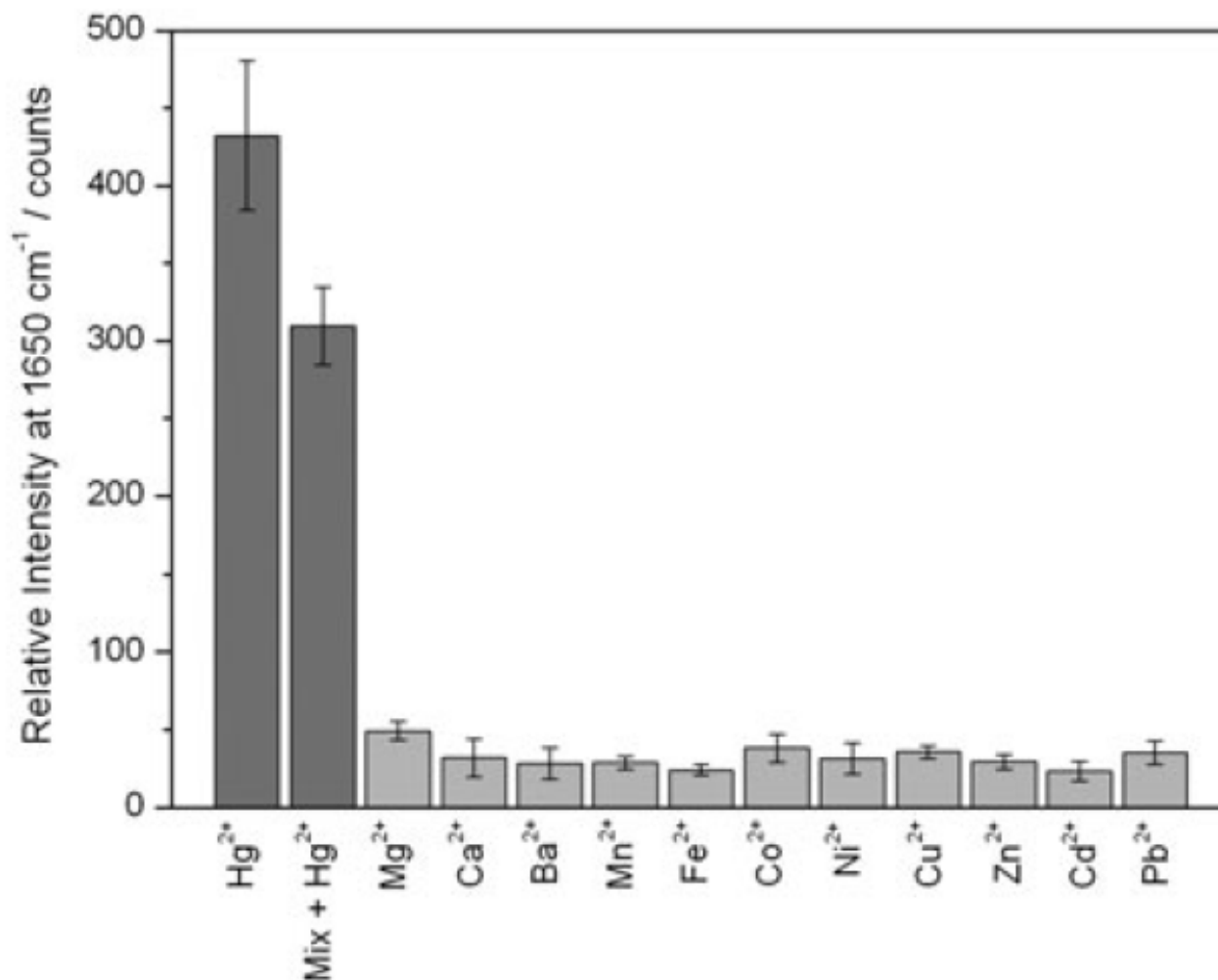


Scheme of transferring and placing a single DNA-modified gold microshell on the point of interest. An optical microscope image shows a DNA-modified single gold microshell at the end of a micropipette tip. The SERS spectrum was obtained from the DNA-modified single gold microshell after reaction with 5 mL of the 10 mM Hg^{2+} ion solution.



SERS spectra obtained from DNA-modified gold microshells at a variety of Hg^{2+} ion concentrations. The most prominent peak of TAMRA is observed at 1650 cm^{-1} . Inset: An optical microscopic image of DNA-modified gold microshells placed on a slide glass. The laser probe is indicated by an arrow. Scale bar in an inset is 10 μm .

Selectivity of SERS probe over various divalent metal ions



Selectivity of SERS probe over various divalent metal ions (10 mM for Hg²⁺ and 50 mM for other metal ions) and a mixture of metal ions (10 mM each of Mg²⁺, Ca²⁺, Ba²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺ plus Hg²⁺).

Summary

- SERS micro-probe for the detection of mercury(II) ions based on a single DNA-modified gold microshell.
- Even though the underlying principle is simple, the results are clear and show sensitive and selective mercury(II) ion detection, as demonstrated by the detection limit of 50 nM and negligible response to other metal ions.
- The DNA-modified single gold microshell can be individually recognized and manipulated under a conventional optical microscope. It can be precisely translocated into a Hg^{2+} ion solution using a typical micropipette and plays the role of a sensitive SERS probe responding to the Hg^{2+} ions in small sample volumes.
- The proposed strategy and analytical method offers a new opportunity for small volume analysis of not only Hg^{2+} ions but also toxic metal ions in environmental and biological samples.

Thanks