Silver, Gold and Copper Nanoparticles for Homeland Security Applications: Surface Enhanced Raman Spectroscopy (SERS) Detection of Explosives and other Threat Chemicals

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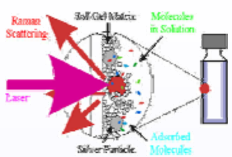
Introduction

Surface-enhanced Raman Spectroscopy (SERS) has been used in our group for several years as a powerful spectroscopic technique for detecting very low concentrations of nitroexplosives in solution.



Inelastic Scattering

State of the Art

Three methods have been extensively used for substrate preparation:

Electron beam lithography (EBL): provides fine control over interparticle spacing and it can be used to generate nanostructures of different shapes. However, it is an expensive and slow method of preparation.

Nanosphere lithography (NSL): are reliable to produce well defied metallic nanoparticles on solid substrates with size and shape tunable optical properties, but it is an expensive and tedious technology

But Colloidal suspensions
Synthesis of nanoparticles via wet chemical method

Provides an inexpensive and versatile approach to metal nanoparticle fabrication

It is one of the group's favorite routes toward the cost effective large scale production of nano-building blocks

Challenges

- Shape control
- Transfer nanoparticles to a solid substrates
- Size control
- Monodispersity
- Reproducibility of the SERS substrates

Opportunities for technology transfer

- Trace levels analysis
- Self Assembled of the functionalized nanoparticles on solid substrates: **New sensor development**

The new studies in the Research, Development, Education and Training twin Centers are focused on the formation of aggregated nanoparticles on glass for transitioning from aqueous media to solid state detection using SERS substrates with high reproducibility.

Experimental and Results

Preparation of SERS Substrates

- **Cu**: Spheres
- **Au**: Spheres, Nanorods, Nanocubes
- **Ag**: Spheres, Triangles
- **Ag/Au**: Spheres

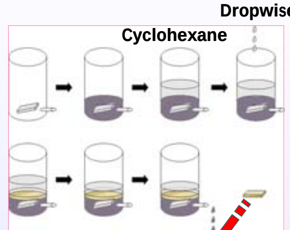
Gold nanorods

9.75mL CTAB 0.1M
250µL $HAuCl_4$ 0.01M
600µL $NaBH_4$ 0.01M

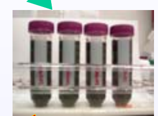
seed

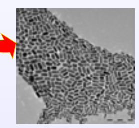
CTAB 0.1 M $AgNO_3$ $HAuCl_4$ Ascorbic Ac Seed

Ethanol Dropwise



Self Assembled





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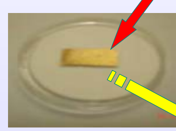
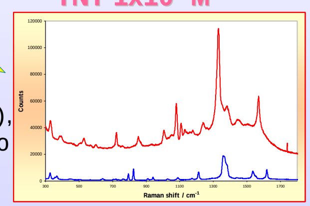


SERS experiments
TNT 1x10^{-3}M

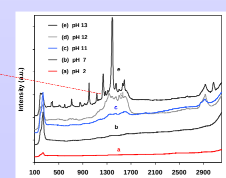


Laser: 785 nm

Principal bands: 1358 cm^{-1} (symmetric nitro stretching), 1551 cm^{-1} (asymmetric nitro stretching)

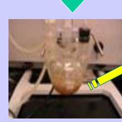
Silver/Gold and Alloys nanospheres

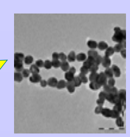
$AgNO_3$ Trisodium citrate, 90 ^{0}C



Laser: 532 nm Power: 10 mW 3 scans

TNT detection via alkaline hydrolysis (indirect form)

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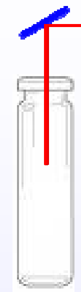
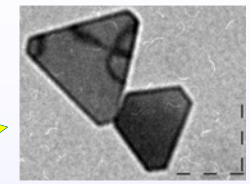
SURFACE ENHANCEMENT FACTORS FOR 2,4,6-TNT DEGRADATION PRODUCTS USING METALLIC COLLOIDS

Colloid	SEF
Au colloid	5.1E+10
Au/Ag colloid	1.4E+11
Ag colloid	2.9E+11

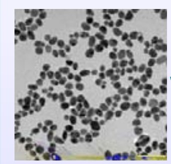
Silver nanoprisms and nanodiscs



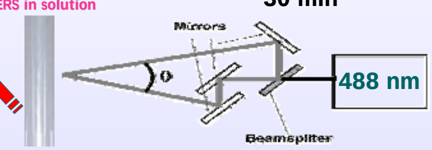


Two Beams

30 min



NEXT STEP: SERS in solution



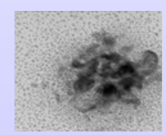
Copper nanospheres

Trisodium citrate $CuSO_4$ $NaOH/NaBH_4$ ⇒ Cu Colloid (mainly spherical seeds) ⇒ Olive green- black solution (different intensities)

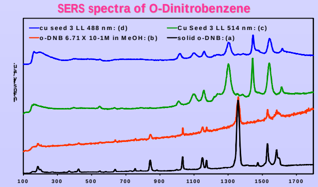
1) Purge with N_2, 2) Ice cold bath 0 °C, 3) 24 hr period

Brown solution (Different Intensities)

TEM



SERS spectra of O-Dinitrobenzene



SERS in solution

Surface Enhancement Factors (SEF) were calculated, the symmetric nitro stretch band at 1307 cm^{-1} and baseline correction was used for the estimation. For 488 nm SEF was ~2x10^2 and ~9x10^3 for 514.5 nm.

The enhancement was attributed to a chemical SERS effect related to charge transfer (CT) between the copper nanoparticles and o-DNB.

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