

National Institute for Research and Development of  
Isotopic and Molecular Technologies



# Metal-coated microsphere arrays: versatile nanofabrication platforms for plasmon-enhanced optical spectroscopy

Cosmin Farcău

11th International Conference of the Balkan Physical Union  
28 August – 1 September 2022, Belgrade, Serbia

# Thanks to...



- Dr. Renaud A. L. Vallee



- Dr. Alina Vladescu



**UNIVERSITATEA  
BABEŞ-BOLYAI**

- Dr. Sanda Boca
- Dr. Ioan Botiz



- Dr. Elizaveta Vereschagina
- Dr. Karolina Milenko



**UMF**  
UNIVERSITATEA DE  
MEDICINĂ ŞI FARMACIE  
**IULIU HAȚIEGANU**  
CLUJ-NAPOCA

- Prof. Ede Bodoki
- Dr. Bogdan-I. Cezar
- Rebeca Moldovan



- Dr. Grigory Arzumanian
- Dr. Kahramon Mamatkulov



- Dr. Alexandra Falamas
- Dr. Valer Tosa
- Dr. Lucian Barbu
- Dr. Nicoleta Tosa
- Denisa Cuibus
- Dr. Daniel Marconi
- Dr. Alia Colnita



# Acknowledgement

## ➤ RO-NO-2019-0517

Nanostructured microfluidic analytical platform for dual SERS-electrochemical detection of emerging environmental pollutants



UMF  
UNIVERSITATEA DE  
MEDICINĂ ȘI FARMACIE  
IULIU HAȚIEGANU  
CLUJ-NAPOCA



Norway  
grants

*uefiscdi*



# Outline

Introduction: Plasmonics and plasmon-enhanced spectroscopy with metal nanostructures

Fabrication of plasmonic nanostructures based on microsphere arrays

Optical properties. Experiment and simulation

Plasmon-enhanced spectroscopy: fundamentals and applications



# Outline

**Introduction: Plasmonics and plasmon-enhanced spectroscopy with metal nanostructures**

Fabrication of plasmonic nanostructures based on microsphere arrays

Optical properties. Experiment and simulation

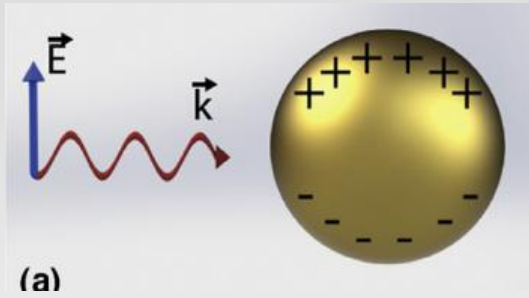
Plasmon-enhanced spectroscopy: fundamentals and applications



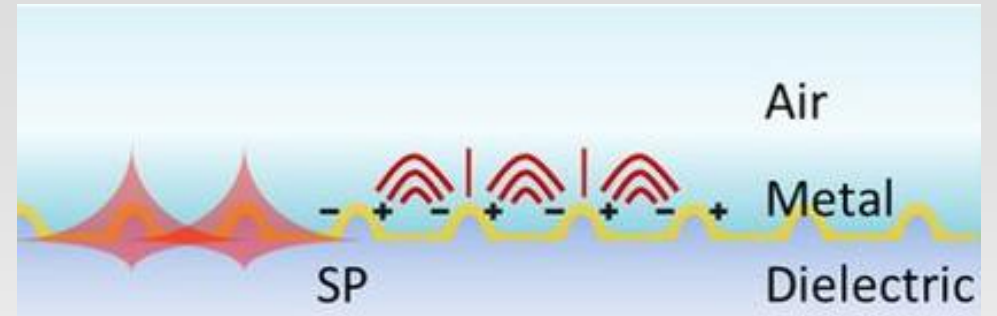
# Introduction

## surface plasmons

localized

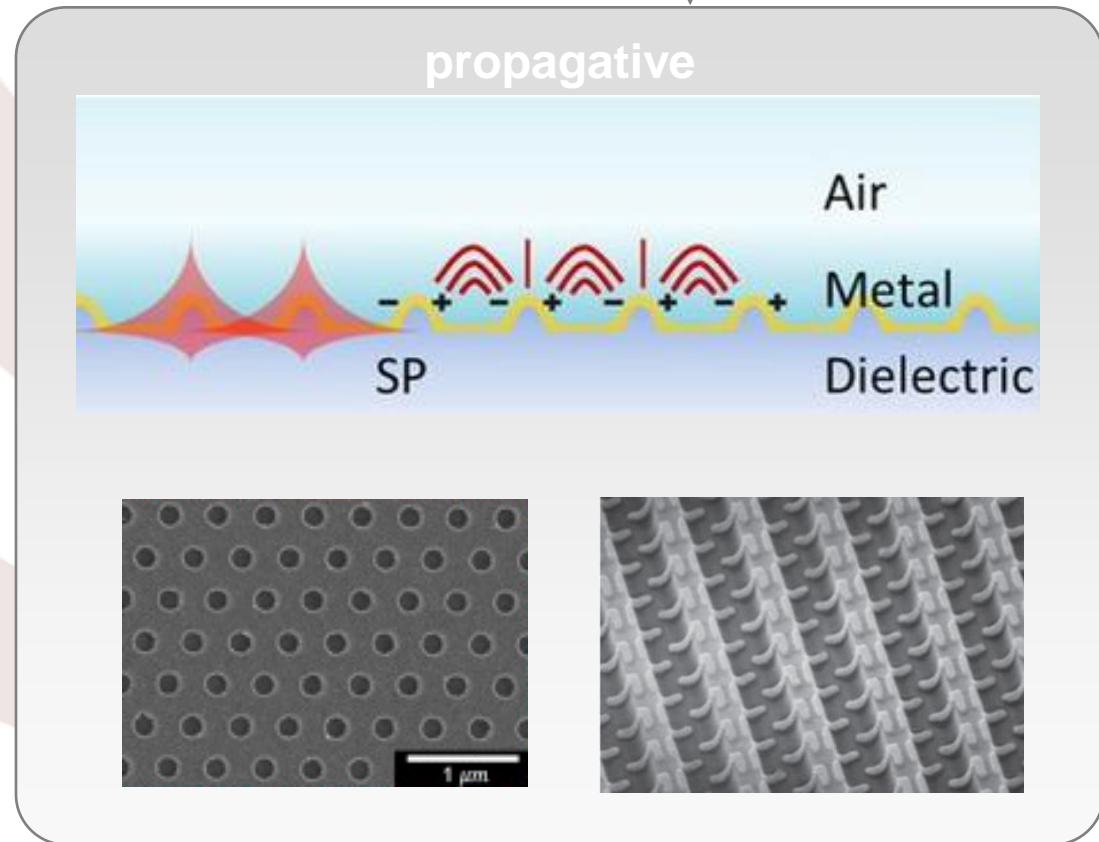
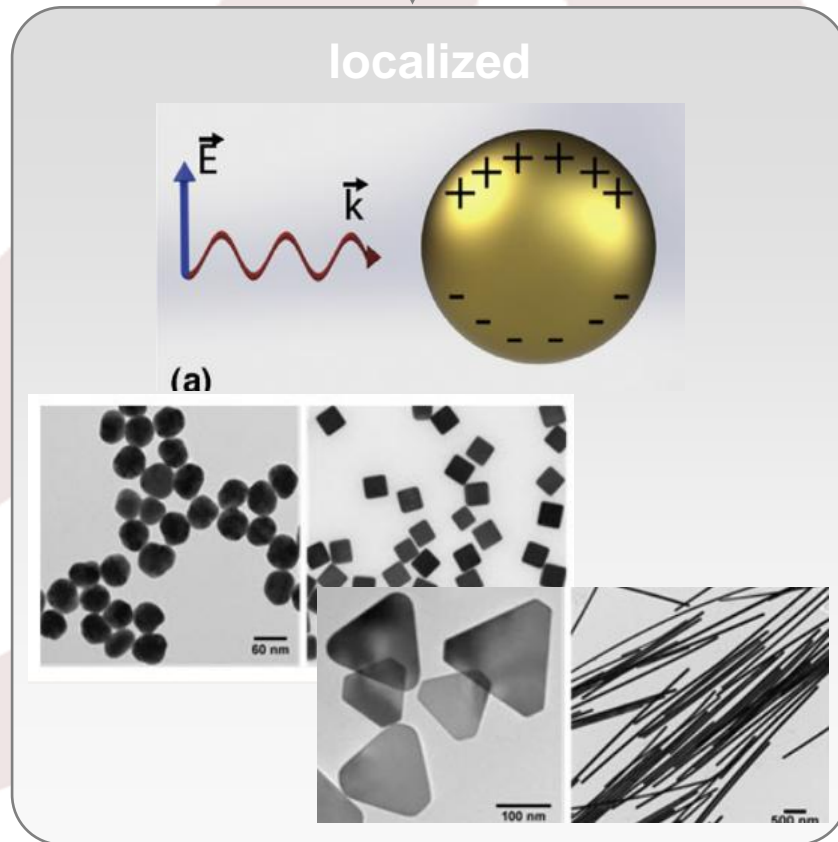


propagative



# Introduction

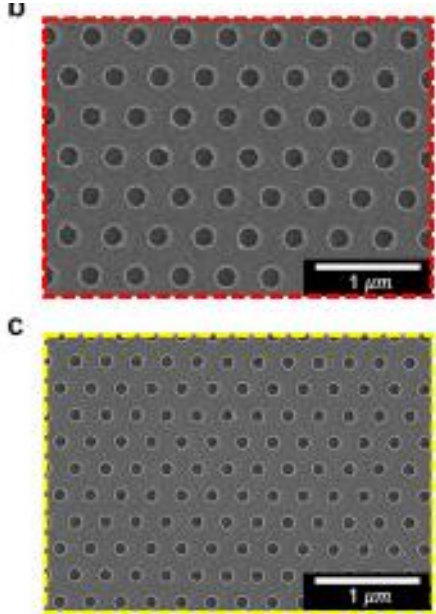
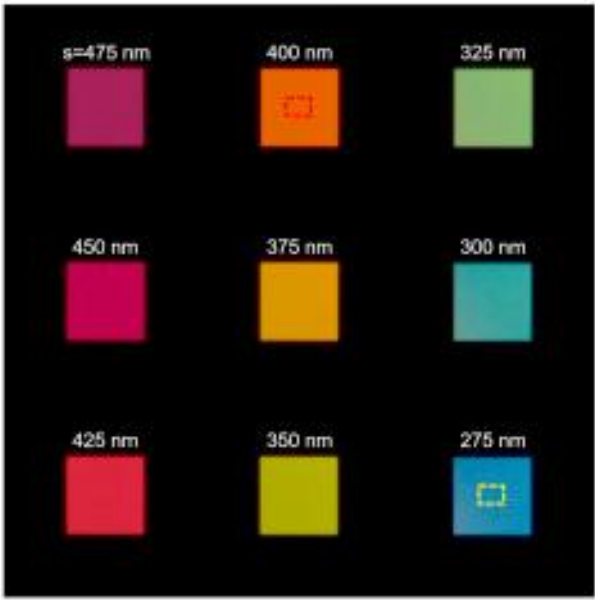
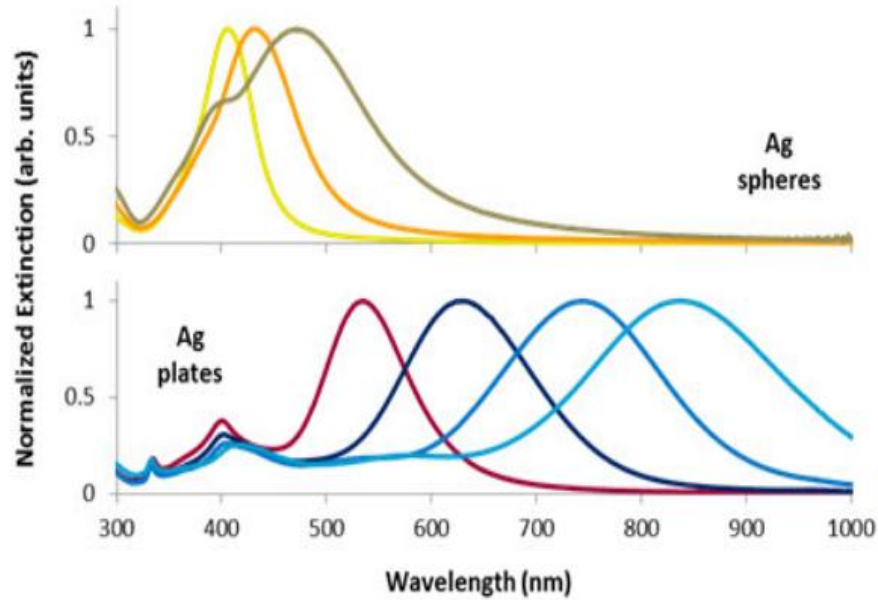
## surface plasmons





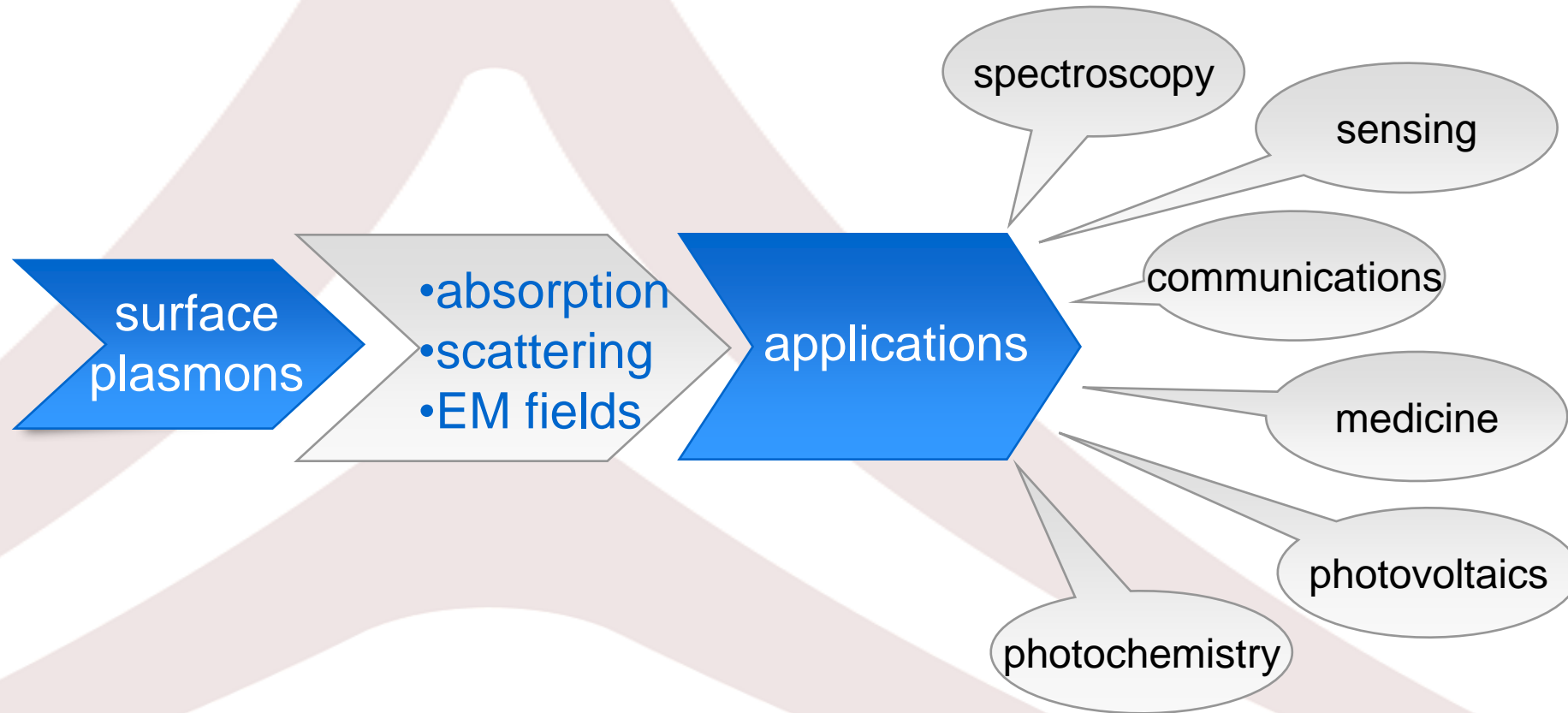
# Introduction

## surface plasmons

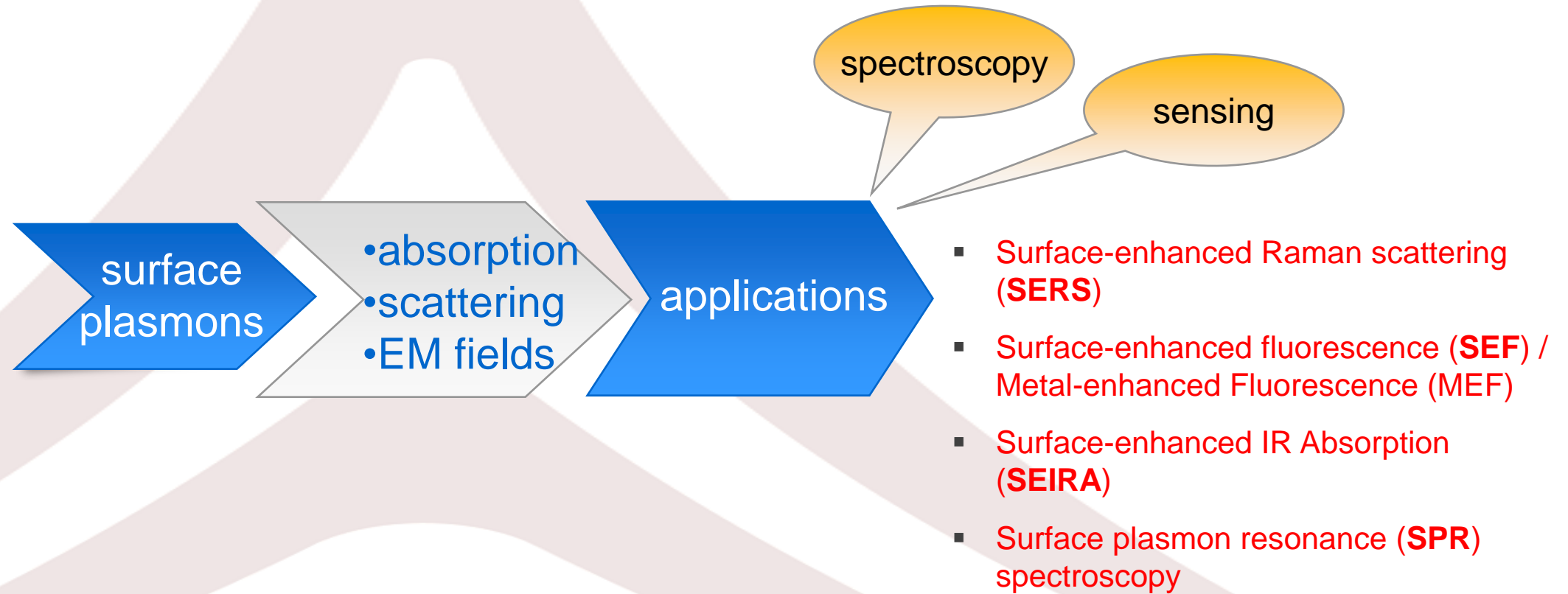




# Introduction



# Introduction



# Outline

Introduction: Plasmonics and plasmon-enhanced spectroscopy with metal nanostructures

**Fabrication of plasmonic nanostructures based on microsphere arrays**

Optical properties. Experiment and simulation

Plasmon-enhanced spectroscopy: fundamentals and applications



# Nanofabrication

## ➤ Fabrication methods:

- Electron beam lithography (EBL); nanoimprint lithography (NIL);

## ➤ Alternative fabrication methods:

- Chemical synthesis
- Colloidal self-assembly
- Colloidal lithography



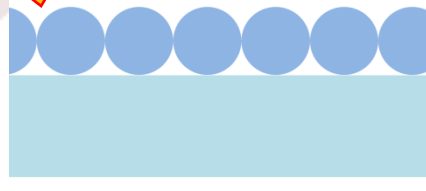
# Nanofabrication

## ➤ Metal-coated microsphere arrays

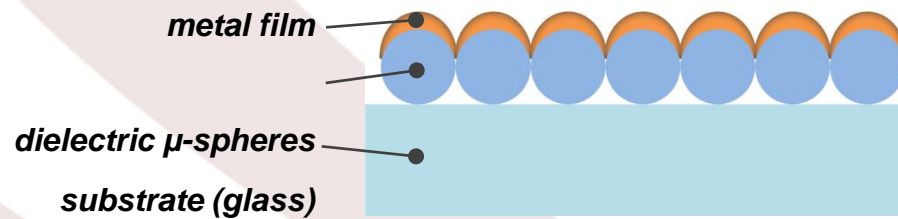
*colloidal self-assembly*



- polystyrene colloids in water;
- diameter 500 nm;
- 2% vol.;

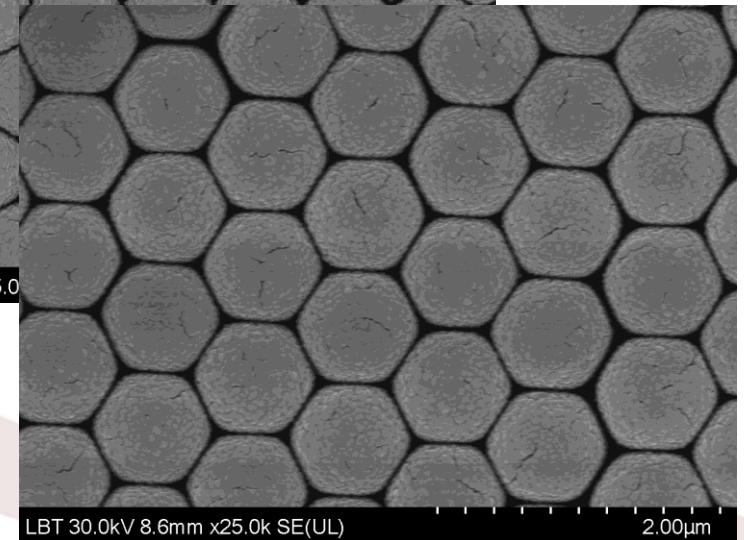
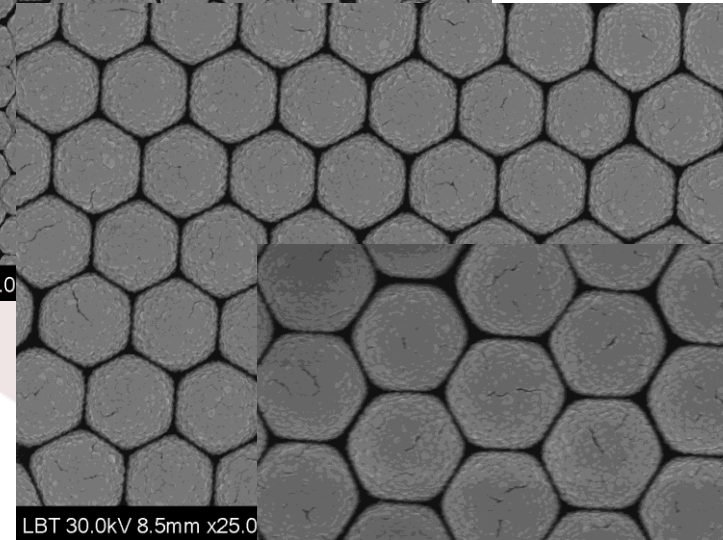
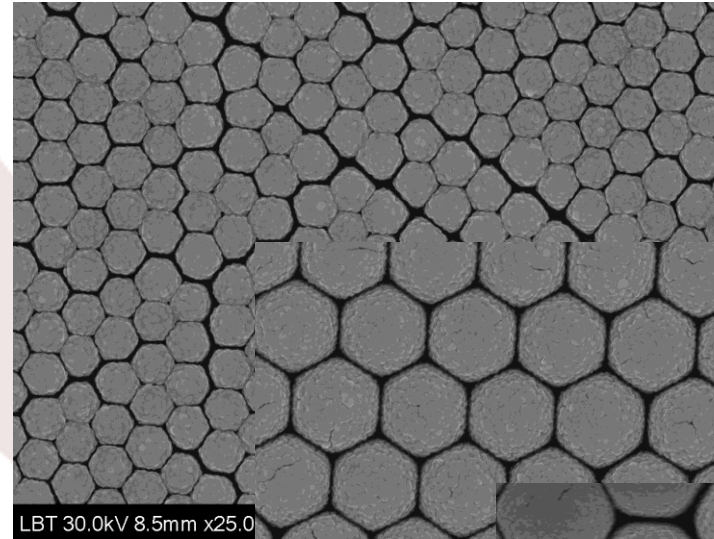
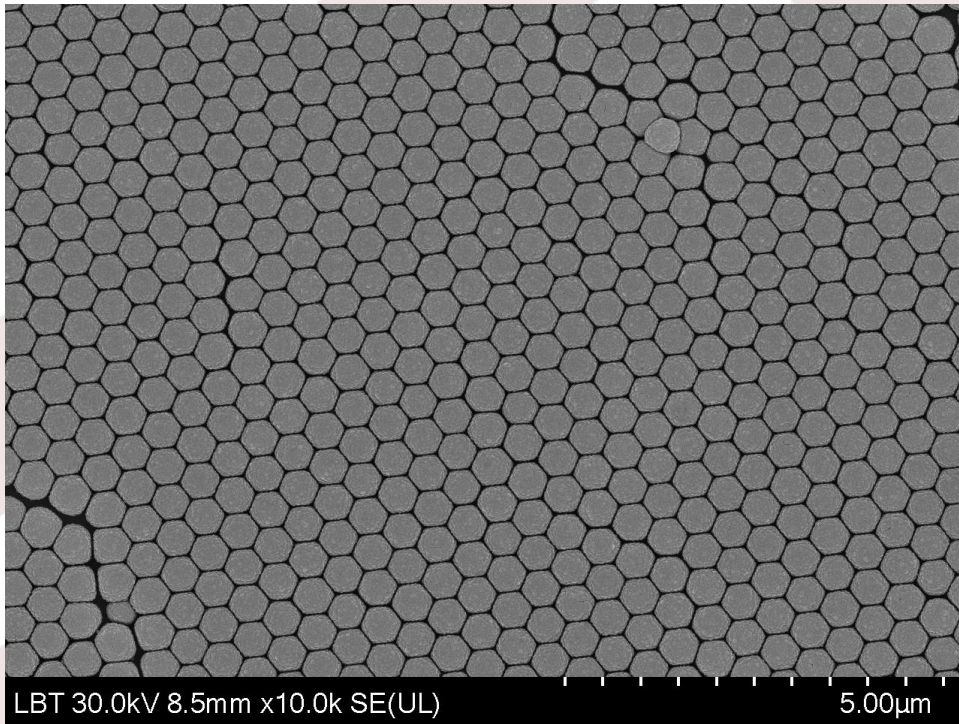


*metal deposition by physical methods*



# Nanofabrication

## ➤ Metal-coated microsphere arrays





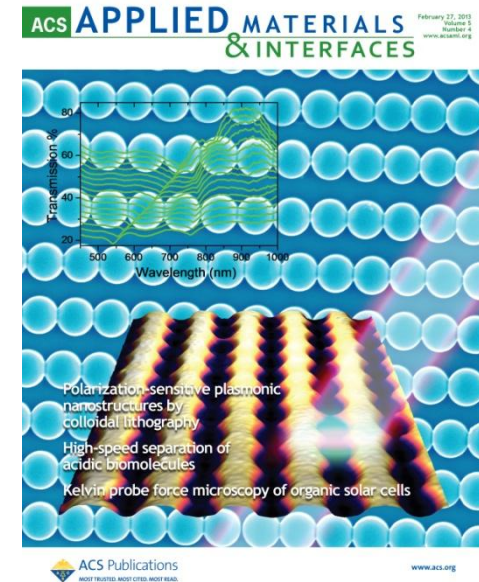
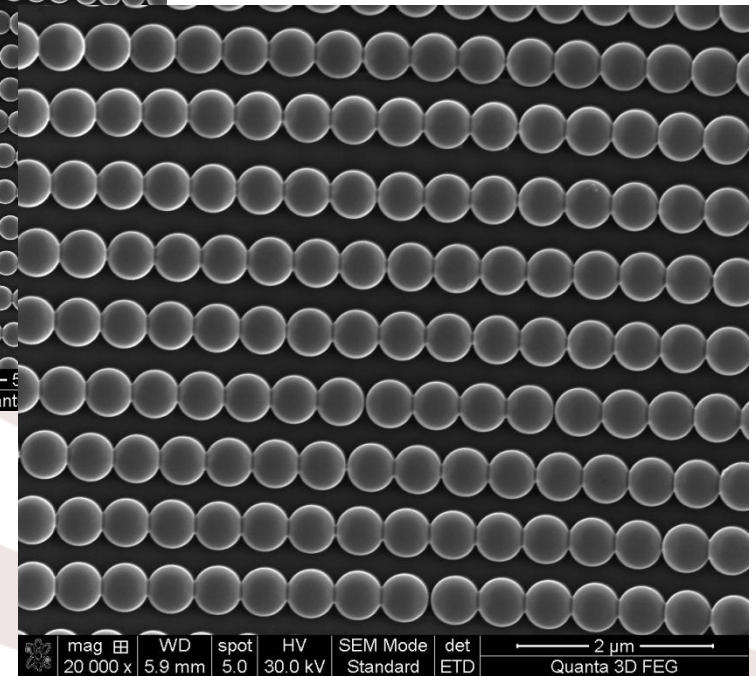
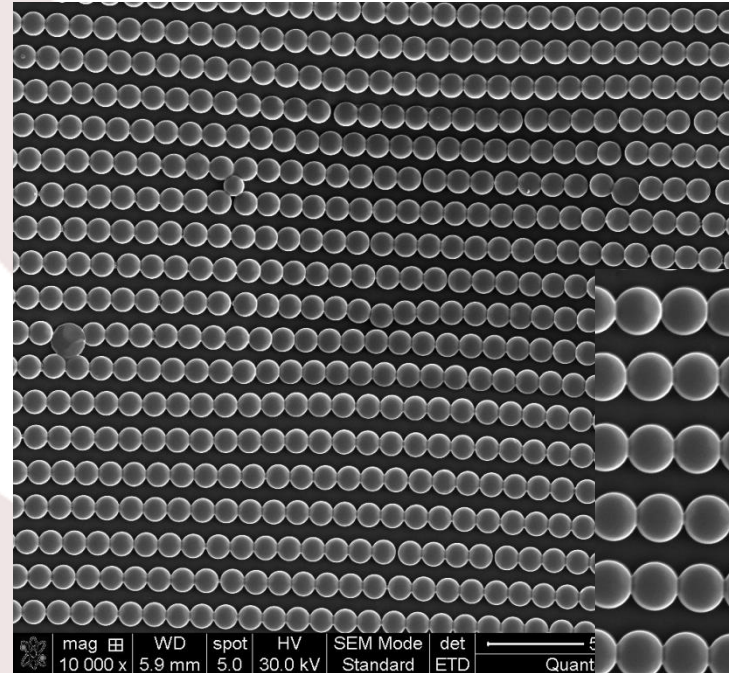
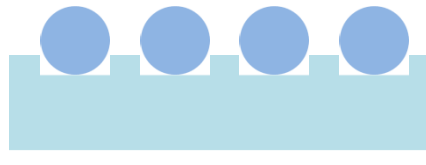
# Nanofabrication

- Linear arrays of metal-coated microspheres

*self-assembly on patterned substrates*



- polystyrene colloids in water;
- diameter 500 nm;
- 2% vol.;



ACS Appl. Mat Interf 2013, 5, 1362.

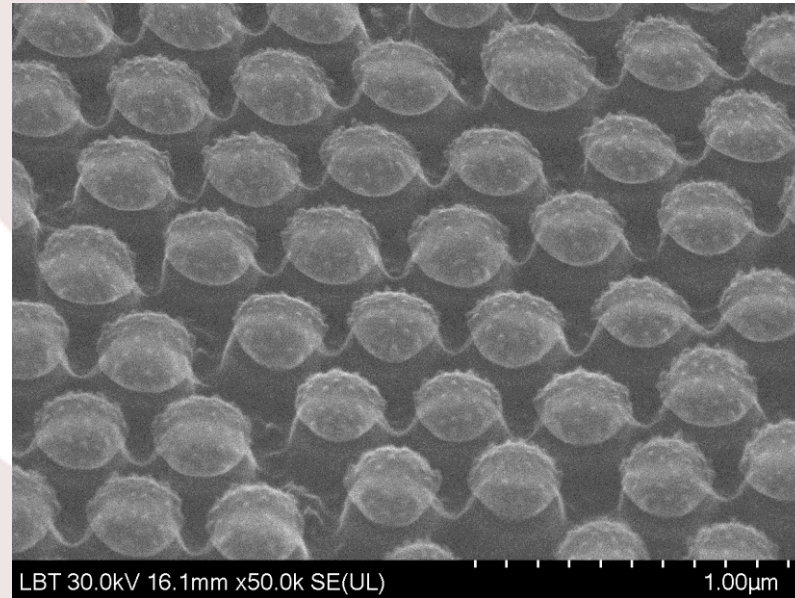
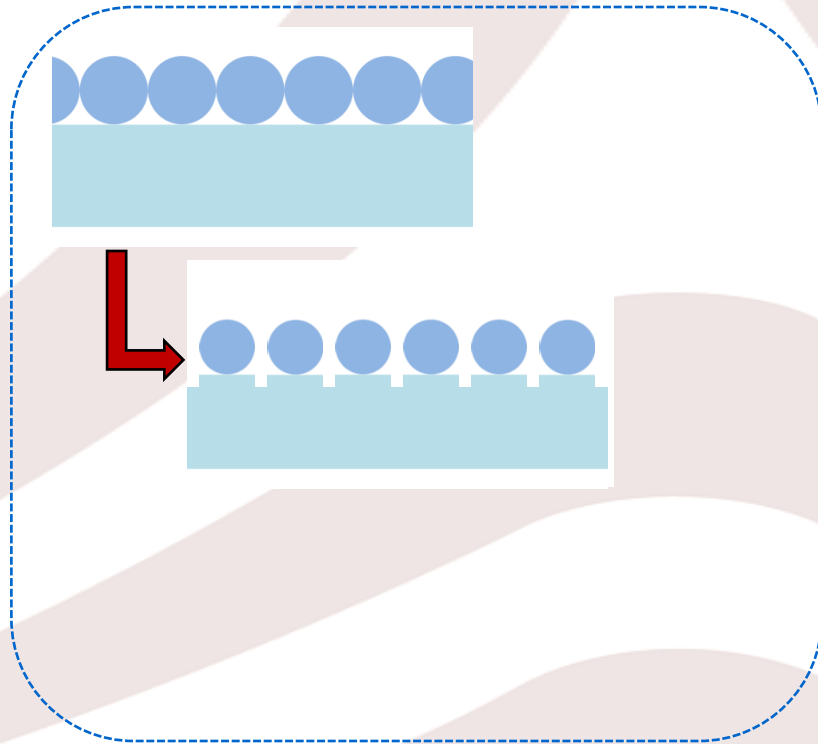




# Nanofabrication

- Microsphere arrays as lithographic masks

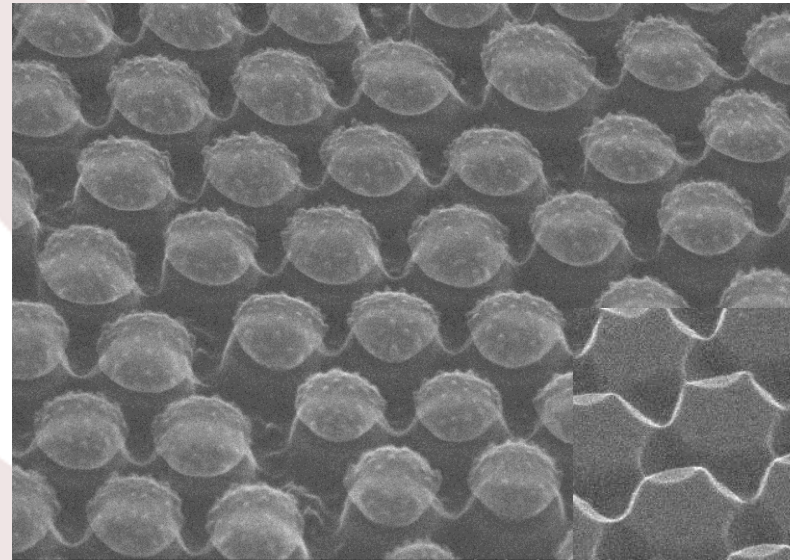
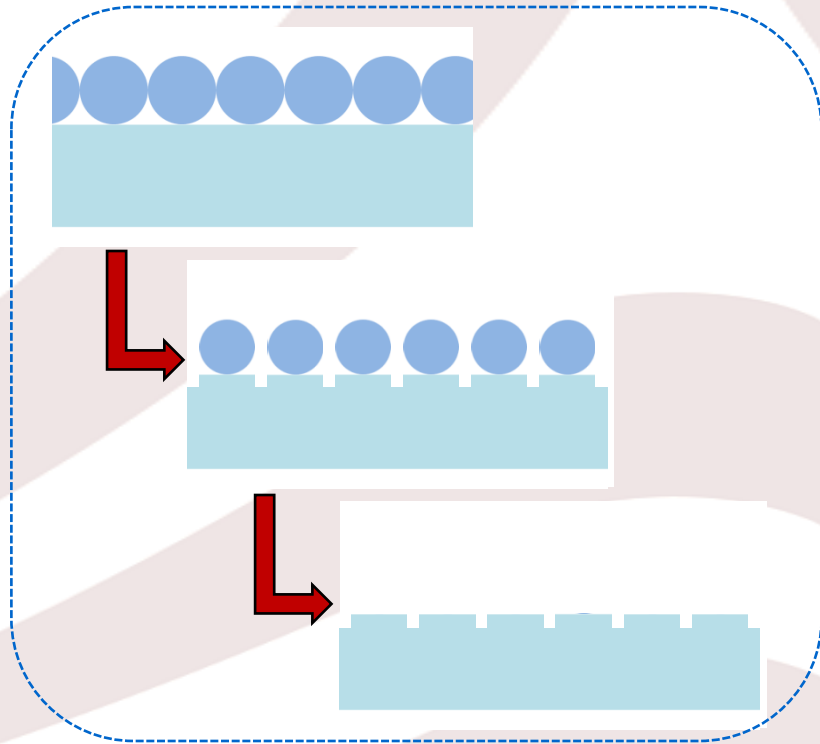
*Plasma etching of microsphere arrays*



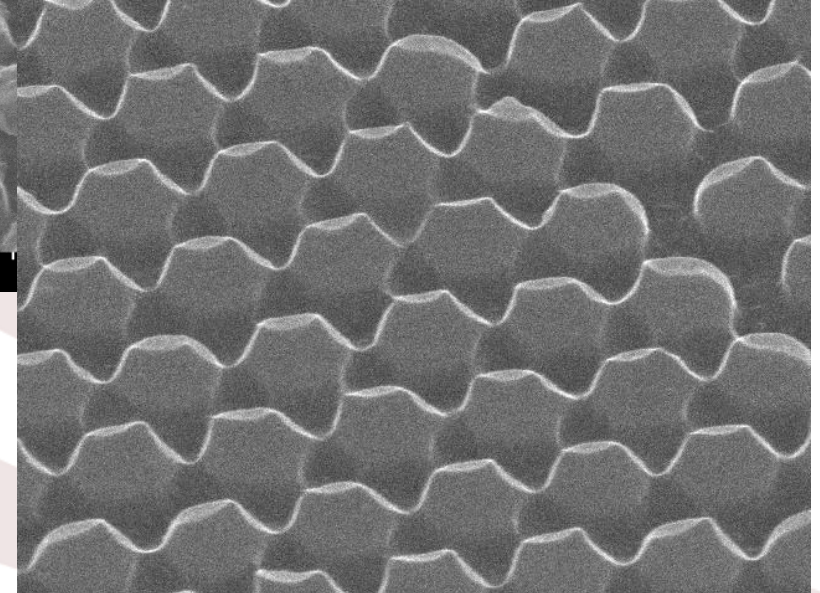
# Nanofabrication

- Microsphere arrays as lithographic masks

*Plasma etching of microsphere arrays*



LBT 30.0kV 16.1mm x50.0k SE(UL)



# Outline

Introduction: Plasmonics and plasmon-enhanced spectroscopy with metal nanostructures

Fabrication of plasmonic nanostructures based on microsphere arrays

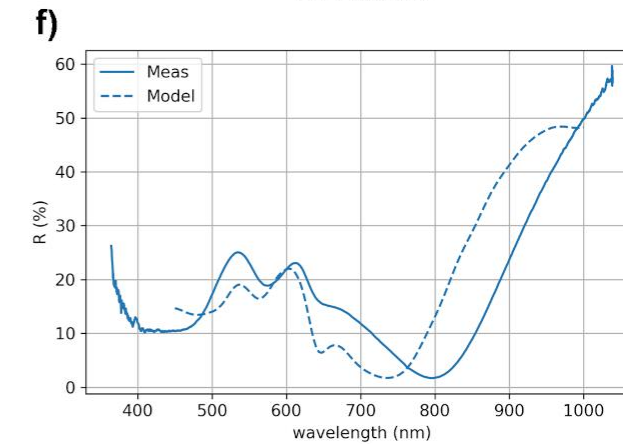
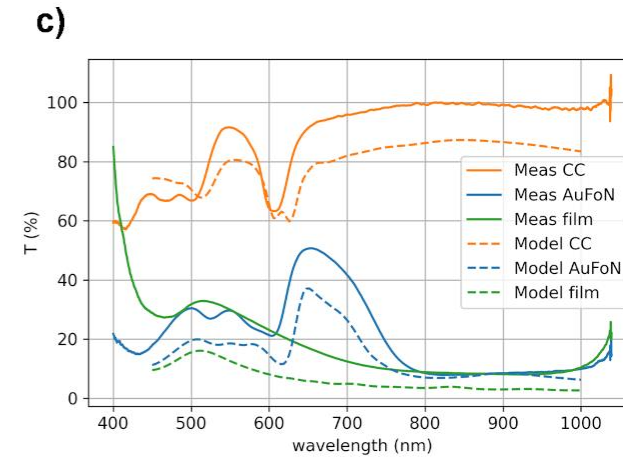
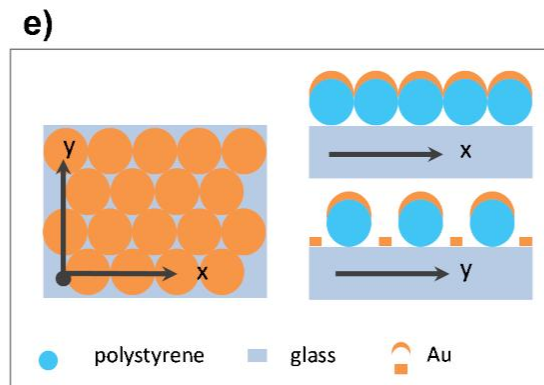
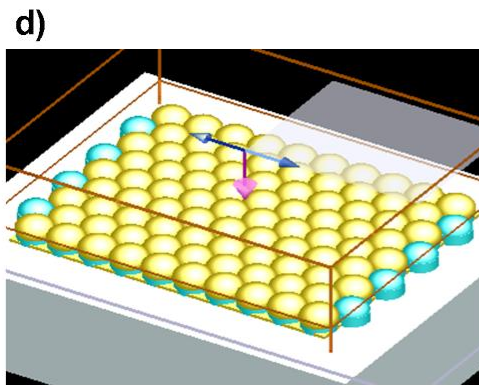
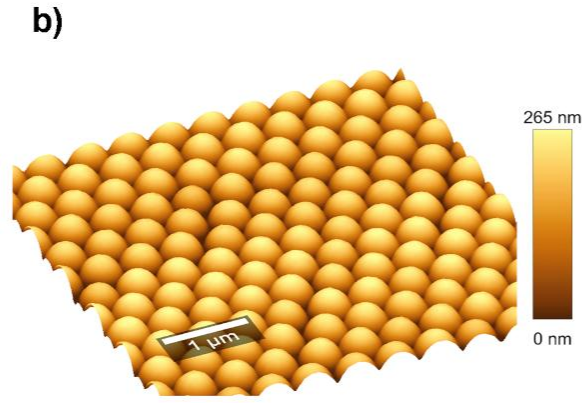
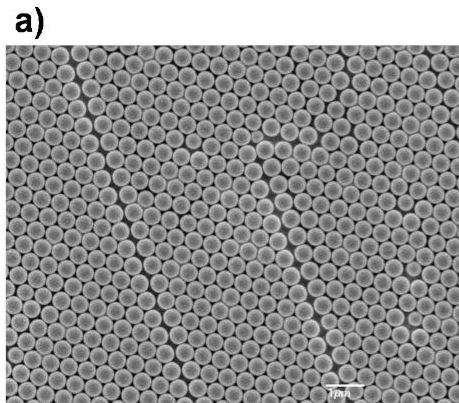
**Optical properties. Experiment and simulation**

Plasmon-enhanced spectroscopy: fundamentals and applications



# Optical properties

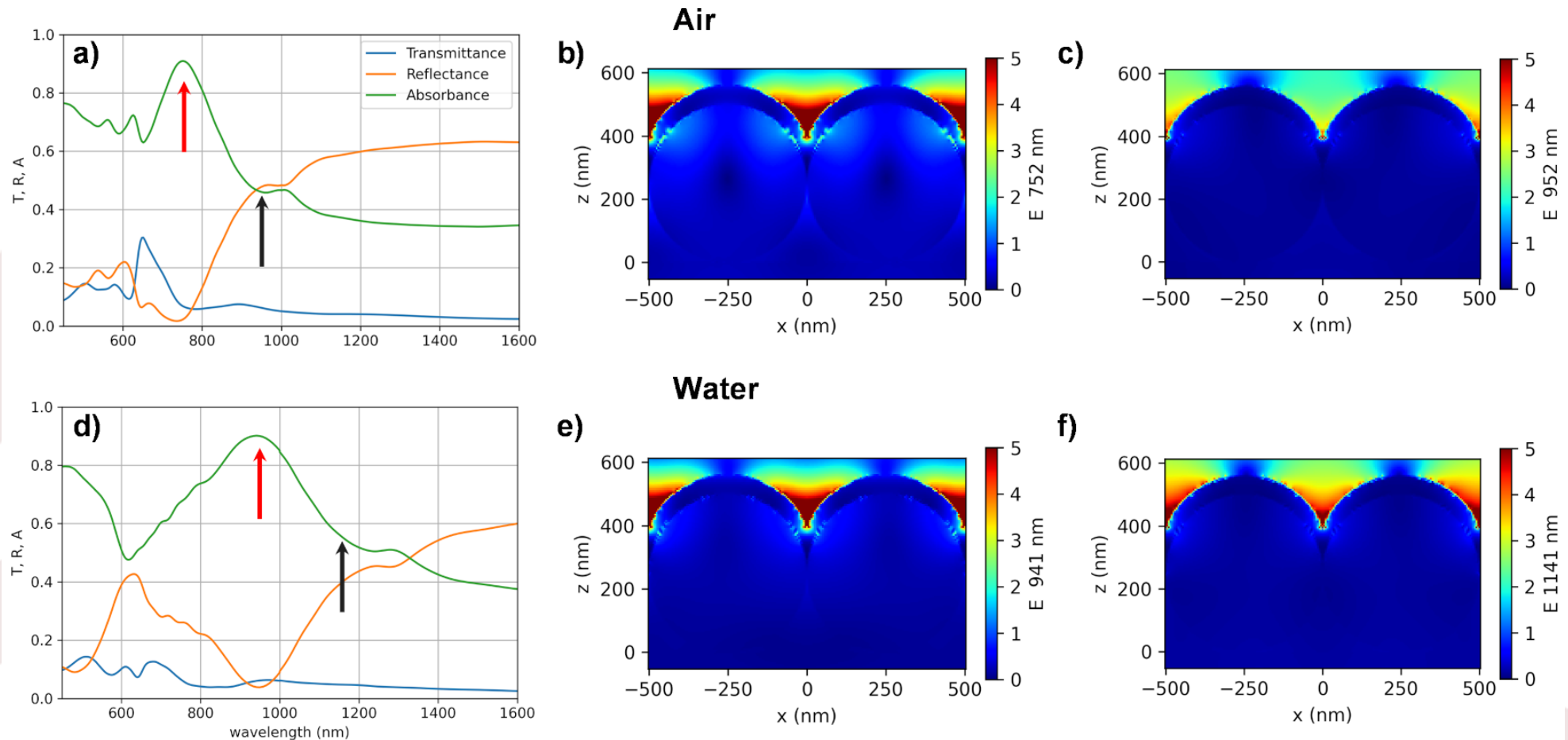
## ➤ Metal-coated microsphere arrays





# Optical properties

## ➤ Metal-coated microsphere arrays

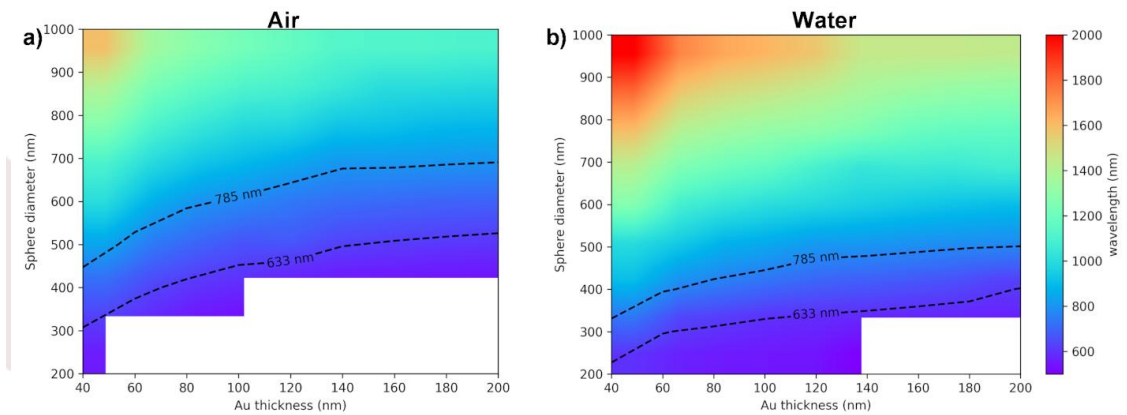
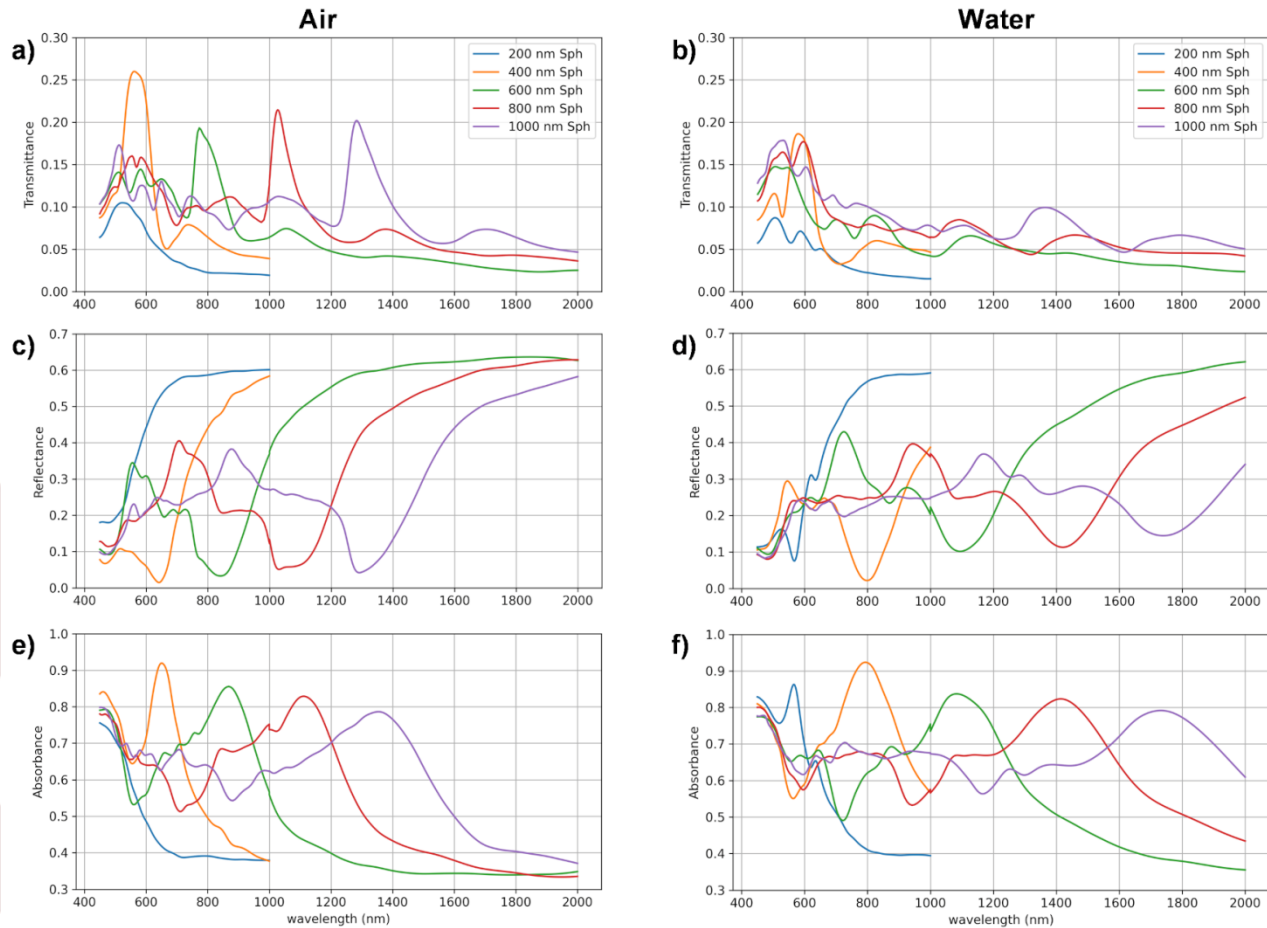


*Opt. Express* 2021, 29, 42238.



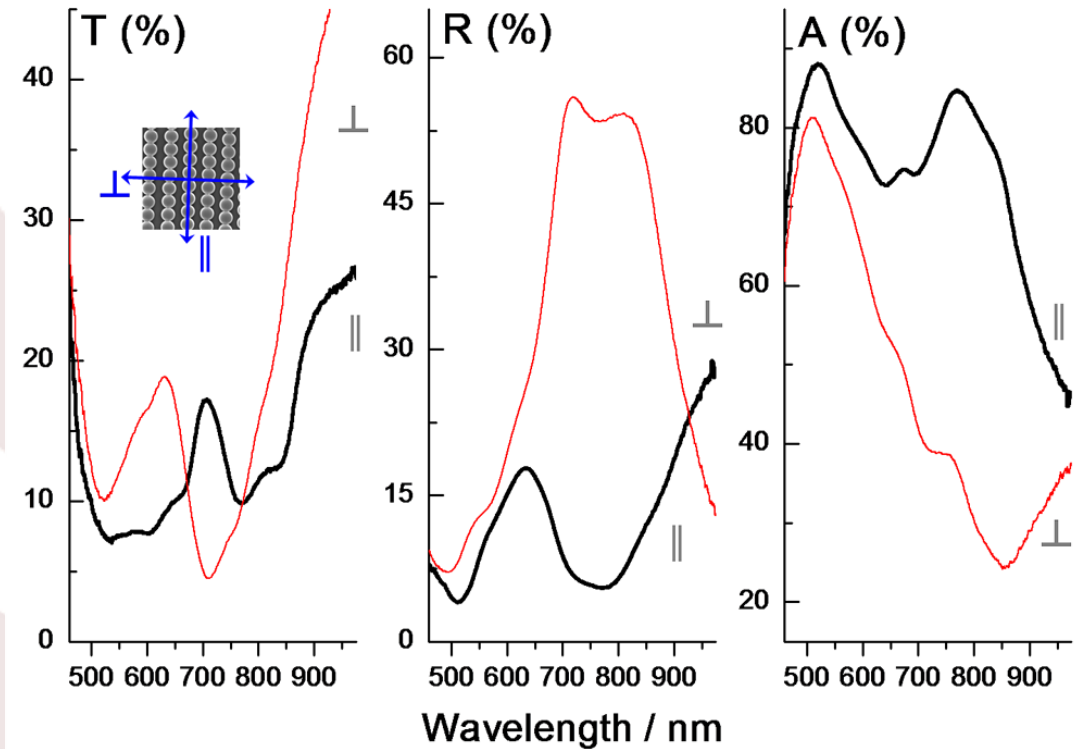
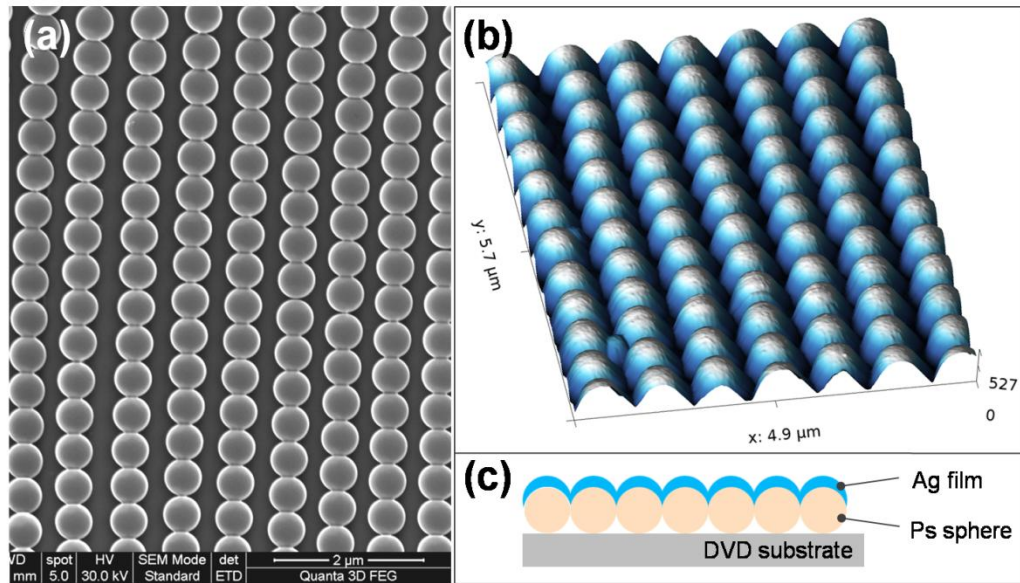
# Optical properties

## ➤ Metal-coated microsphere arrays



# Optical properties

- Linear arrays of metal-coated microspheres





# Outline

Introduction: Plasmonics and plasmon-enhanced spectroscopy with metal nanostructures

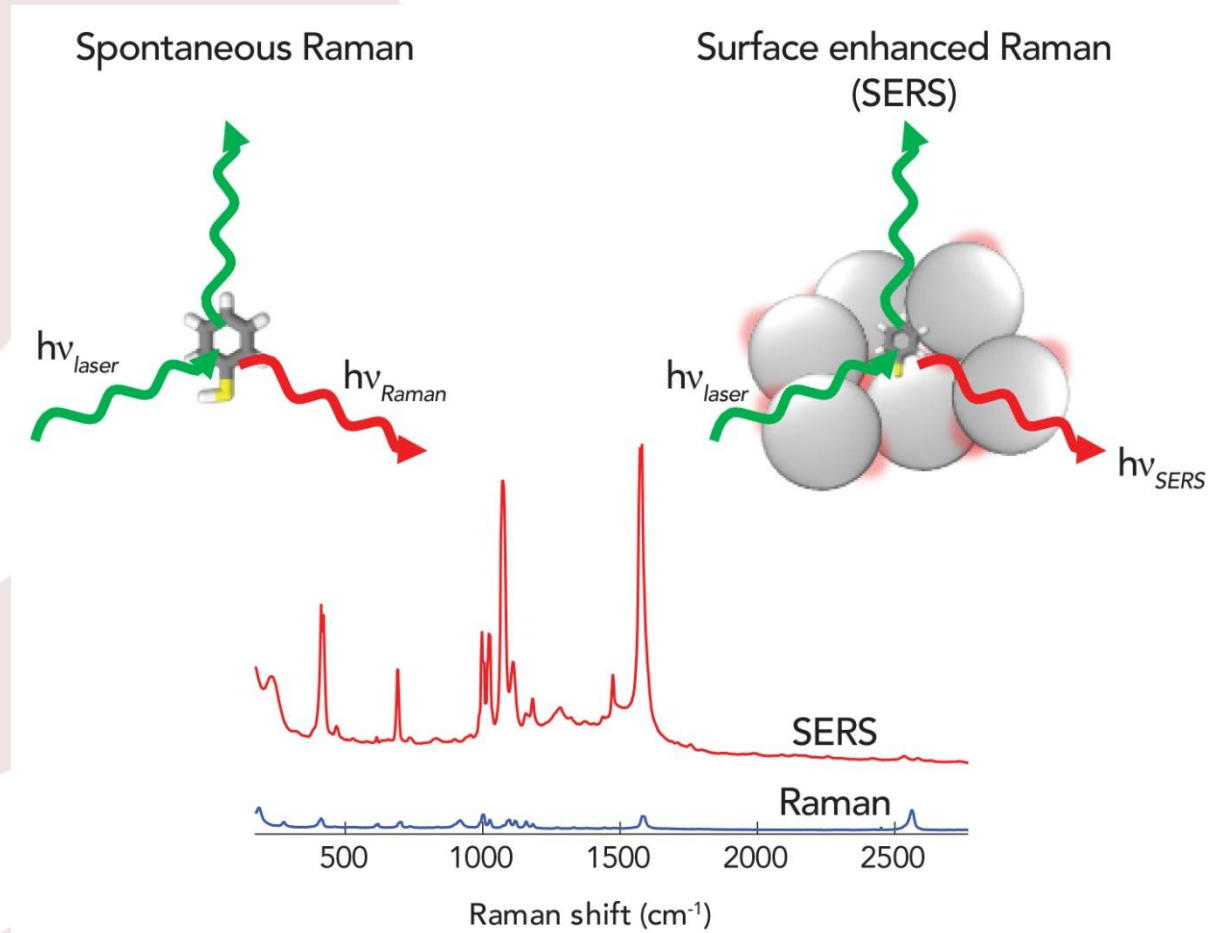
Fabrication of plasmonic nanostructures based on microsphere arrays

Optical properties. Experiment and simulation

**Plasmon-enhanced spectroscopy: fundamentals and applications**



# Surface-enhanced Raman scattering

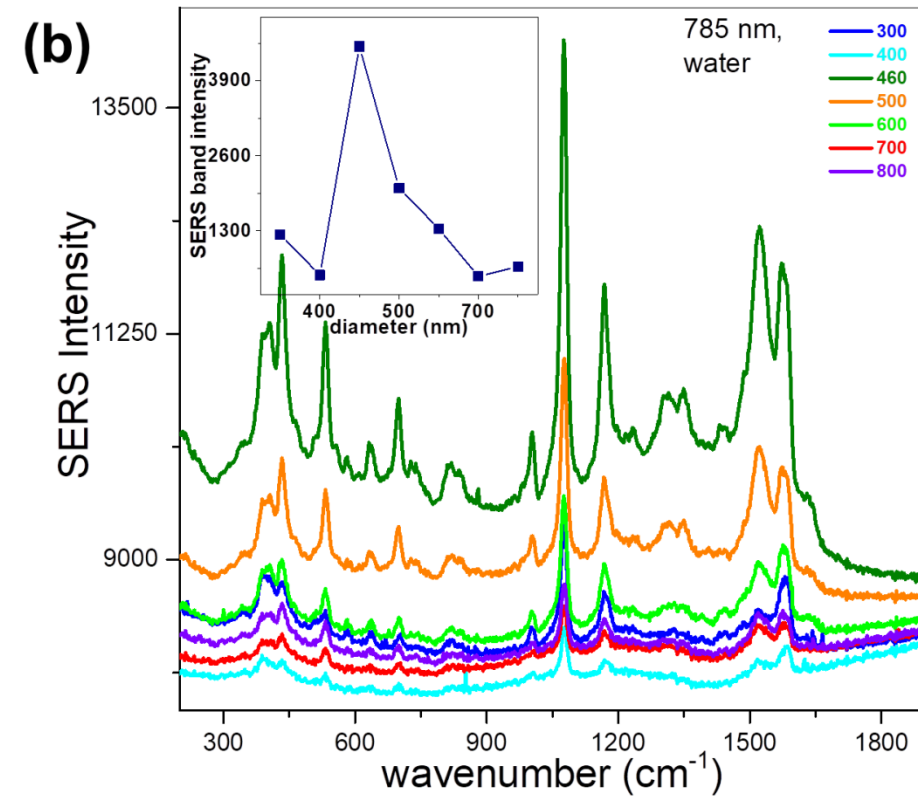
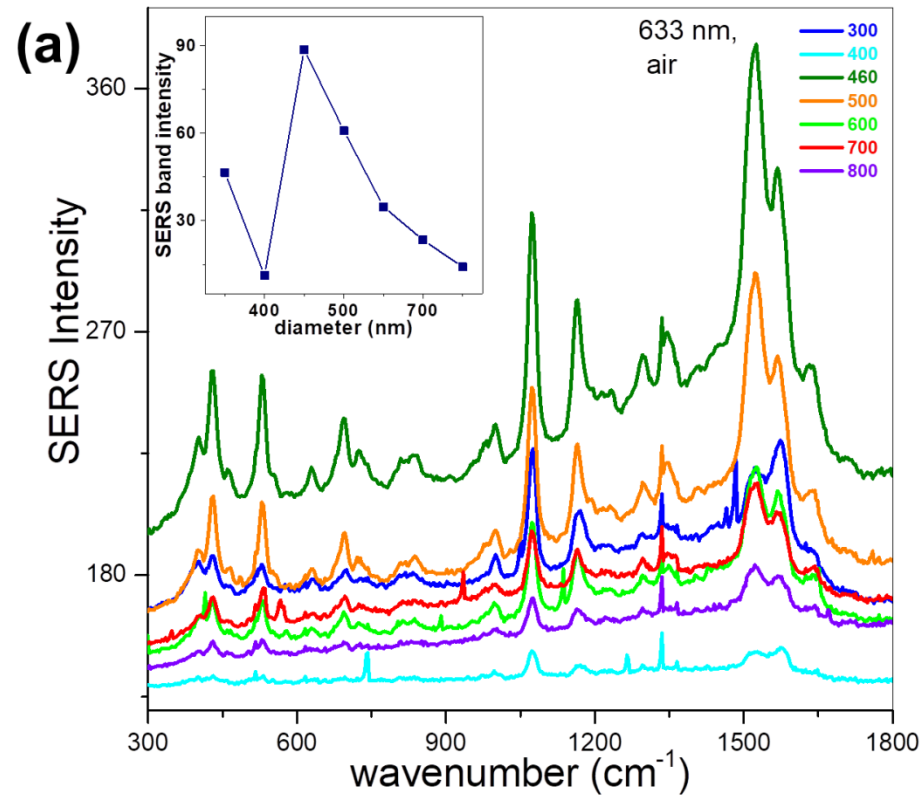


<https://www.spectroscopyonline.com/view/sers-and-TERS>



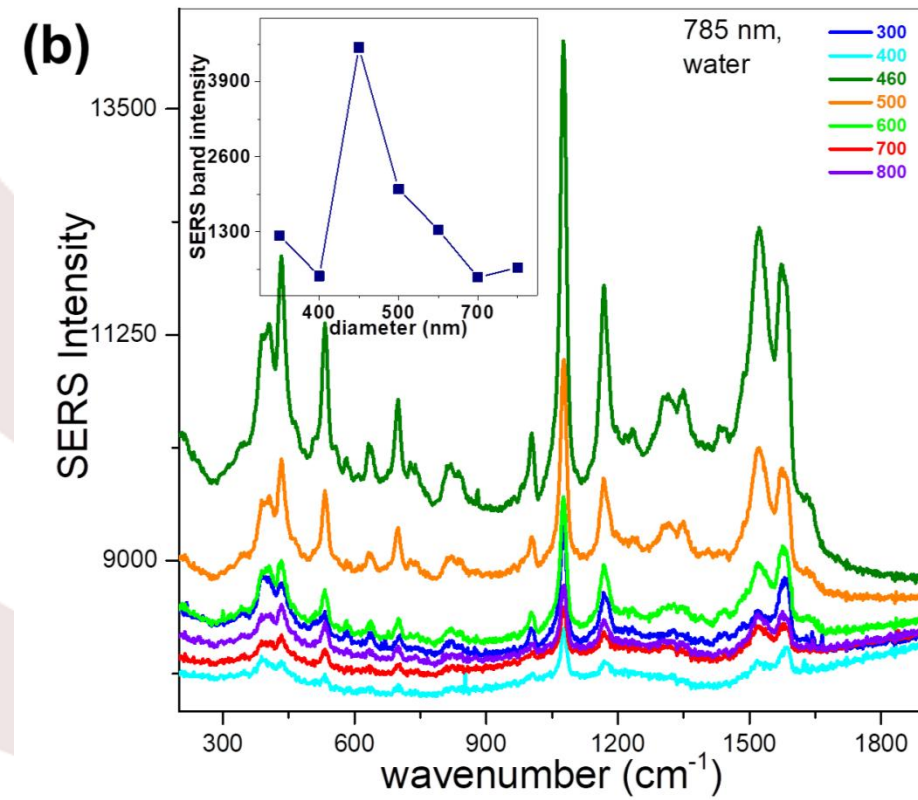
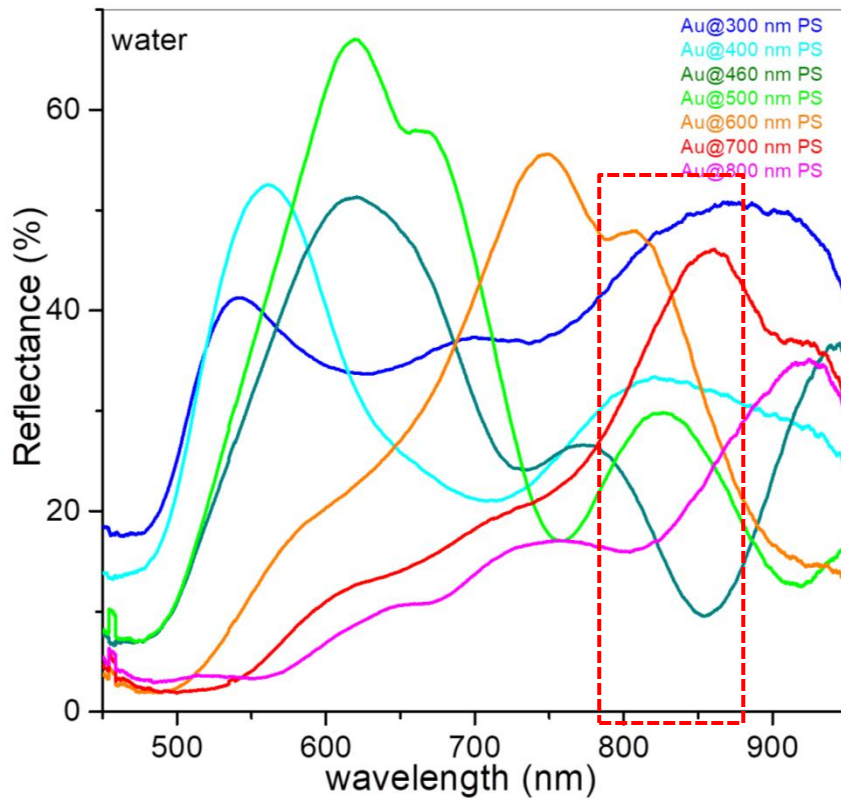
# Surface-enhanced Raman scattering

## ➤ Metal-coated microsphere arrays



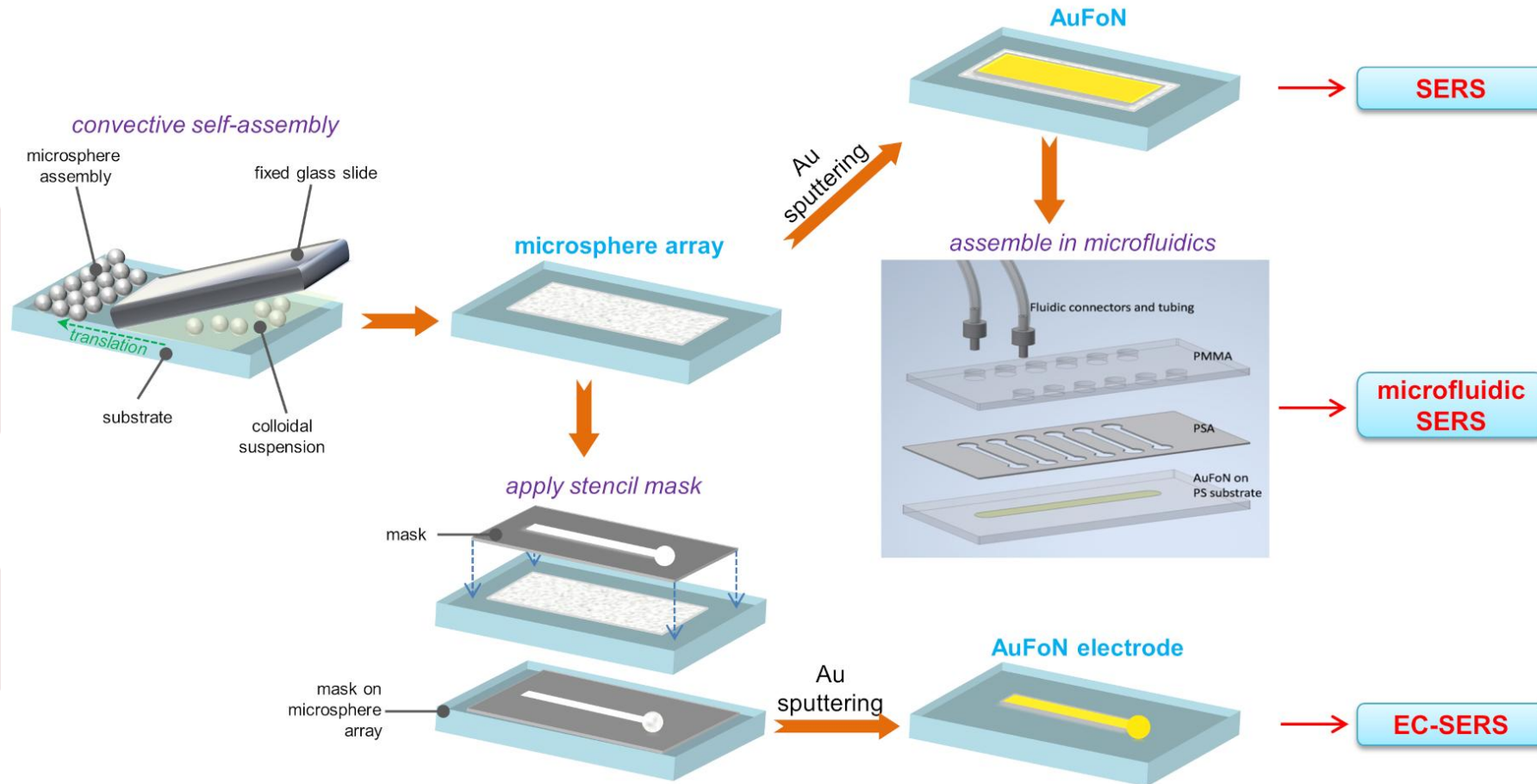
# Surface-enhanced Raman scattering

## ➤ Metal-coated microsphere arrays



# SERS applications

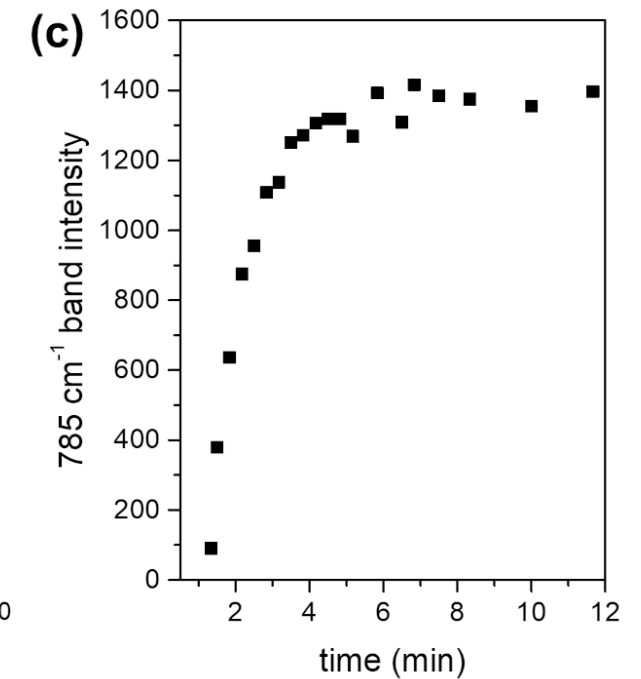
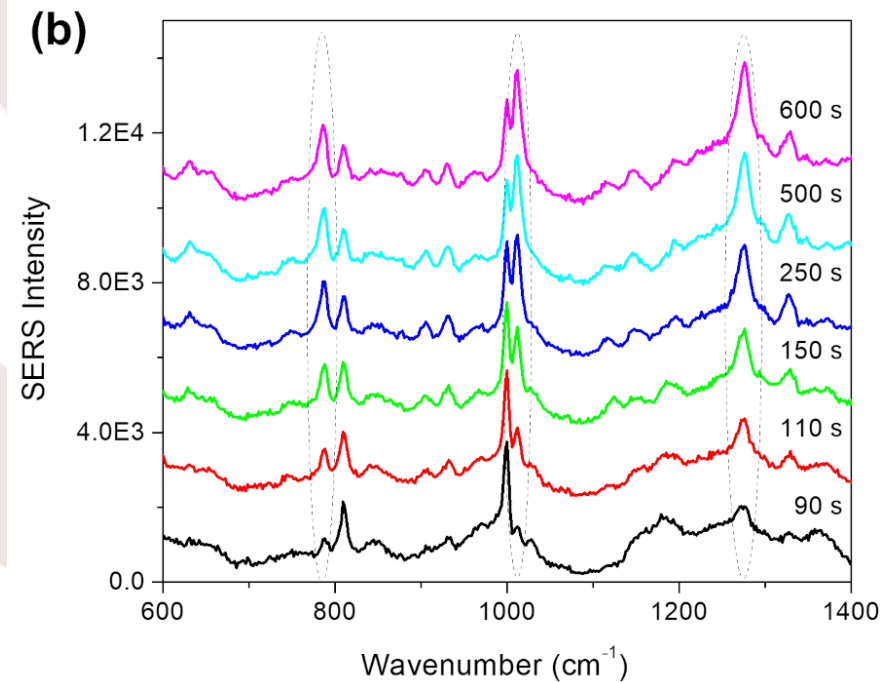
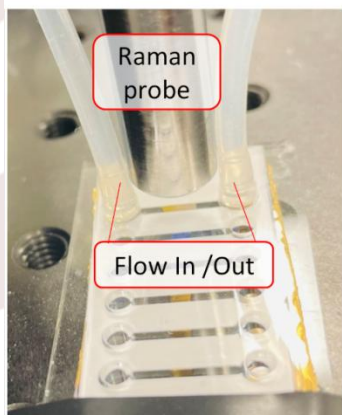
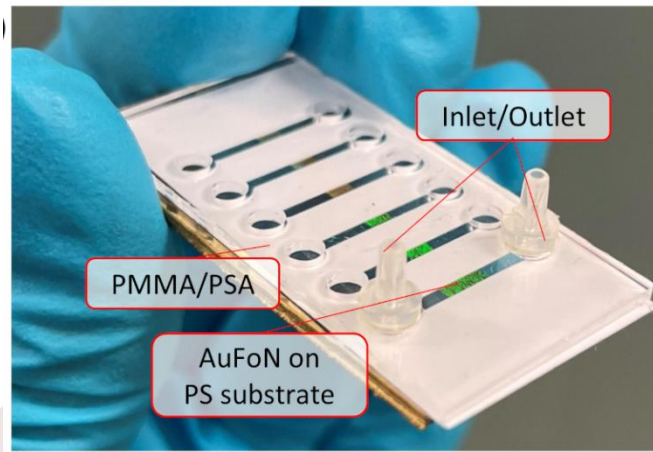
## ➤ Metal-coated microsphere arrays in SERS applications





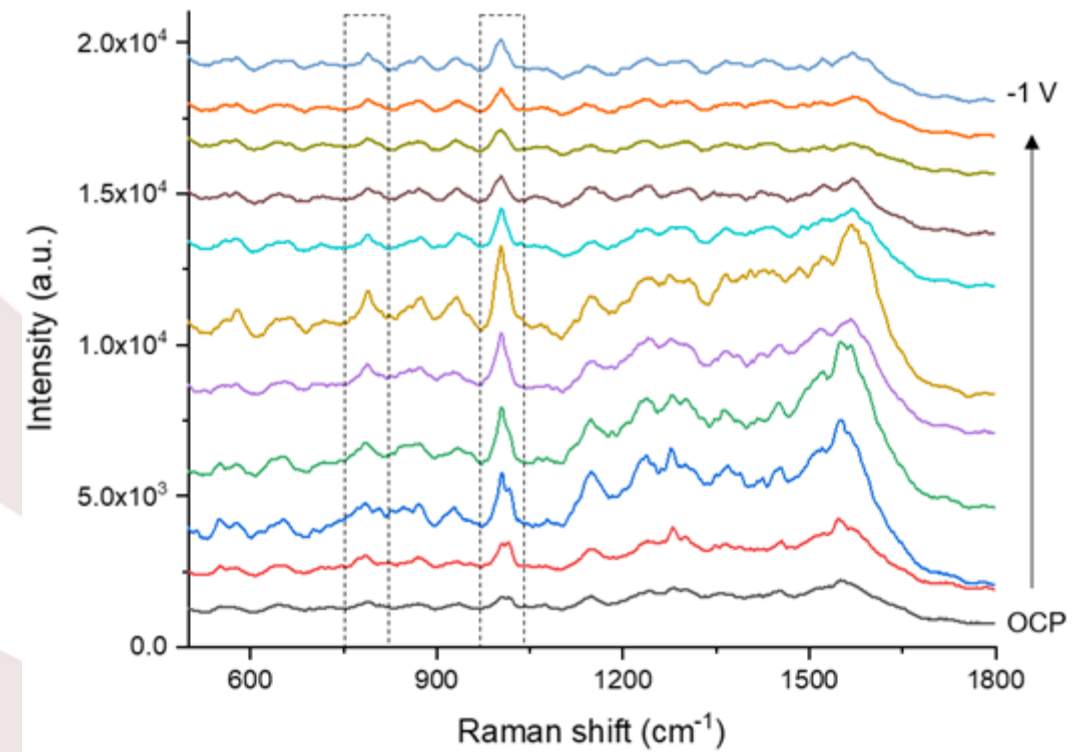
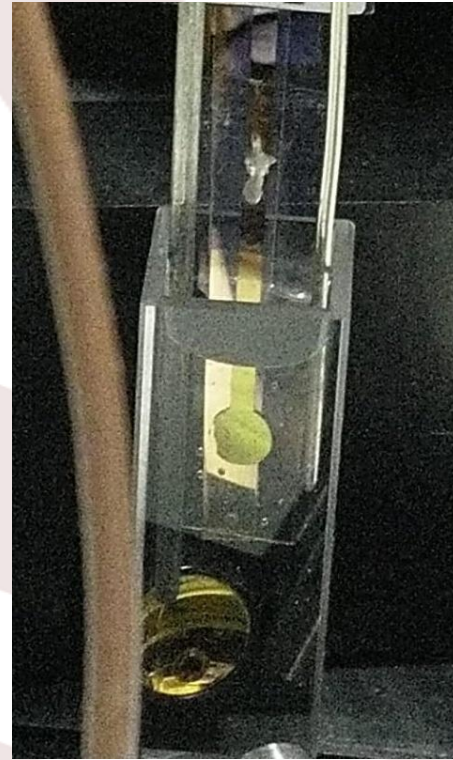
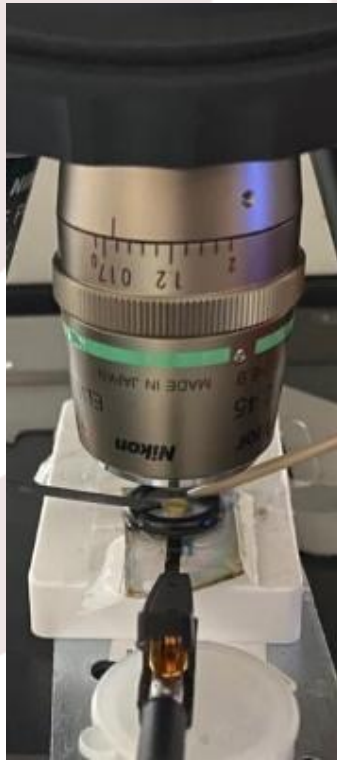
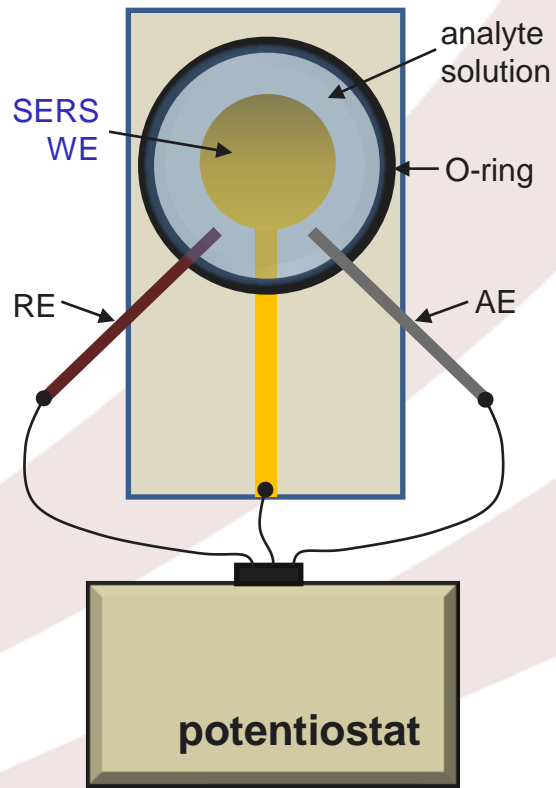
# Microfluidic-SERS

- Metal-coated microsphere arrays in microfluidics



# Electrochemical-SERS

- Metal-coated microsphere arrays as electrodes





# Conclusions

- Self-assembled microsphere arrays are a versatile nanofabrication platform:
  - Metal-coated microsphere arrays;
  - Linear arrays of metal-coated microspheres;
  - Masks for plasma etching
- Optical properties of metal-coated microspheres:
  - Tunable across the visible range;
  - Similar behaviour in air and water;
  - Polarization-sensitive or insensitive;
- SERS application of metal-coated microsphere arrays:
  - Size-dependent, tunable SERS enhancement;
  - Can be integrated in microfluidics;
  - Coupled electrochemical-SERS assays can be developed.

