Development of highly sensitive SERS substrate based on (ZnO, CuO)/Au 1D nanostructures toward applications in environmental and biomedical fields.

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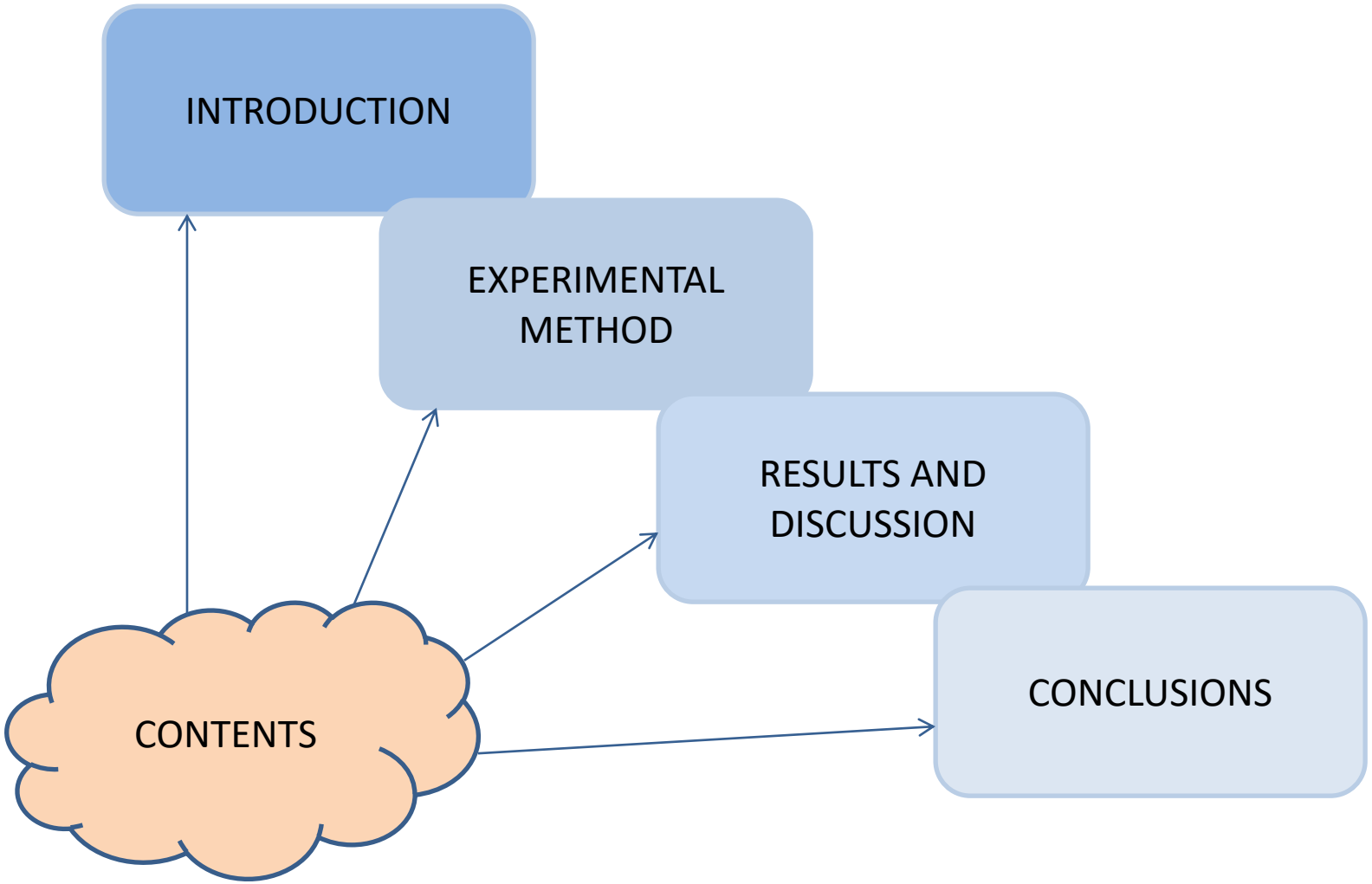
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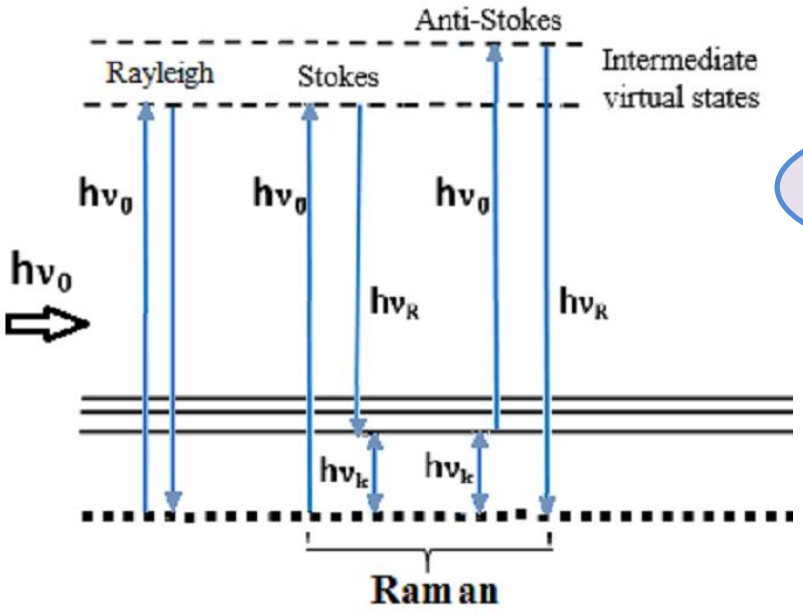
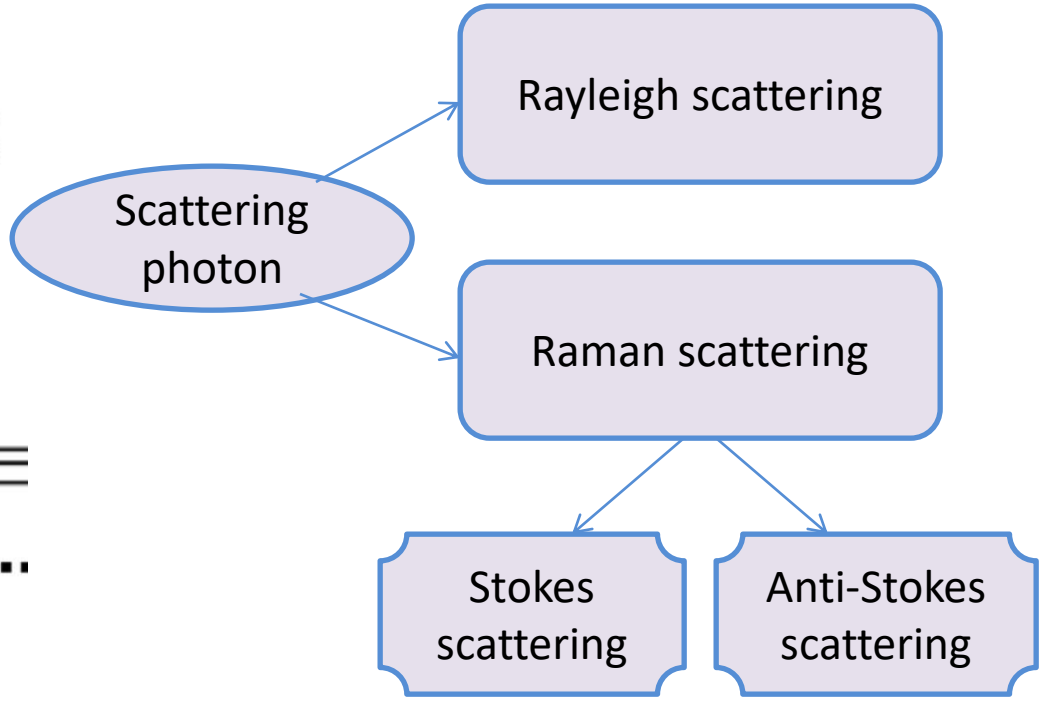
1. Introduction
1.1. Raman effect

- Raman effect or inelastic light scattering effect was first observed by Raman in 1928 which brought Raman the Nobel Prize in Physics in 1930.





Raman Scattering: Classical Picture

Molecule in electric field:

- Charges in molecule move in electric field => dipole is induced

$$\vec{p} = \alpha E$$

-Electromagnetic wave oscillating with incident frequency

$$\vec{E} = E_0 \cos(2\pi\nu_0 t)$$

-Induced dipole proportional to this oscillating field:

$$\vec{p} = \alpha\vec{E} = \alpha E_0 \cos(2\pi\nu_0 t)$$

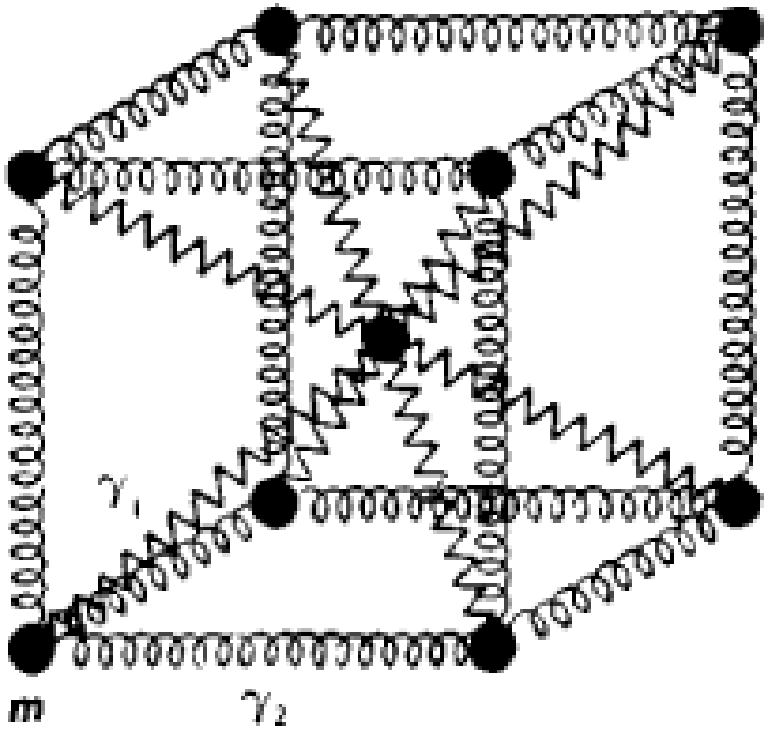
-Polarization also depends on the oscillation of the molecule

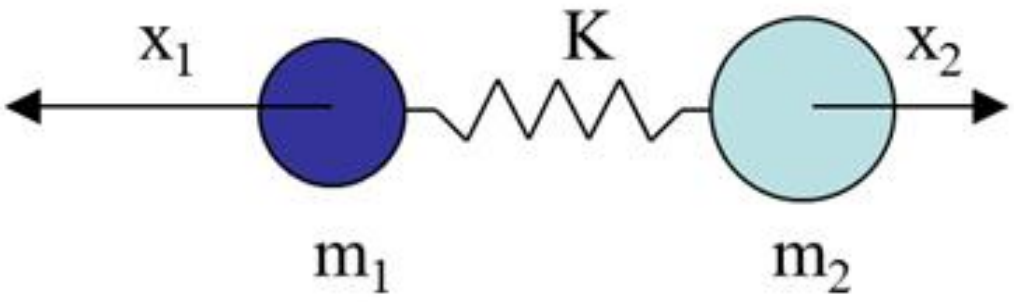
$$dQ = Q_0 \cos(2\pi\nu_{vib} t) \qquad \alpha = \alpha_0 + \frac{\partial\alpha}{\partial Q} dQ$$

Rayleigh Scattering | Stokes Raman | anti-Stokes Raman

$$\vec{p} = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{\partial\alpha}{\partial Q}\frac{Q_0 E_0}{2}(\cos(2\pi(\nu_0 - \nu_{vib})t) + \cos(2\pi(\nu_0 + \nu_{vib})t))$$

ν_0 | $\nu_0 - \nu_{vib}$ | $\nu_0 + \nu_{vib}$





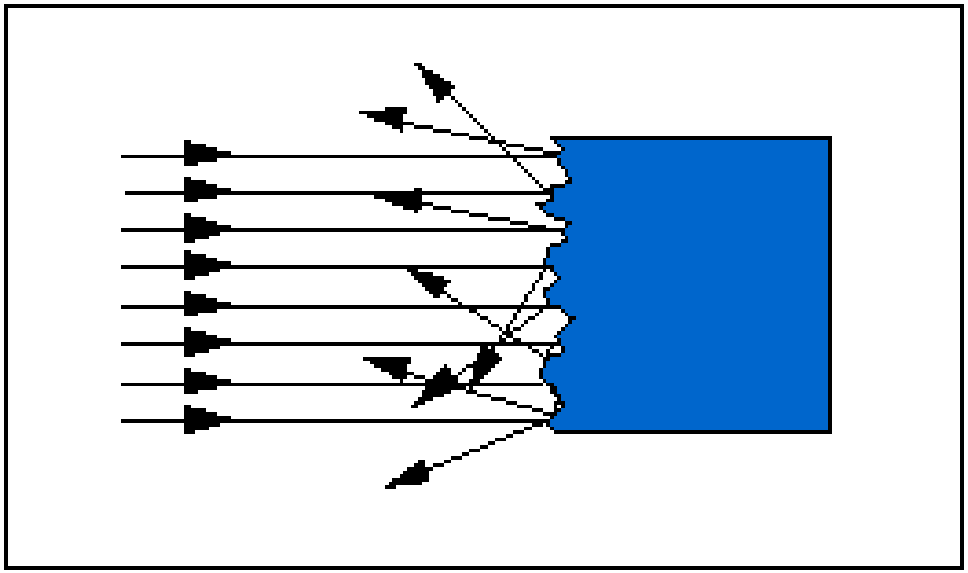
$$\nu_{vib} = \sqrt{\frac{K}{M}}$$

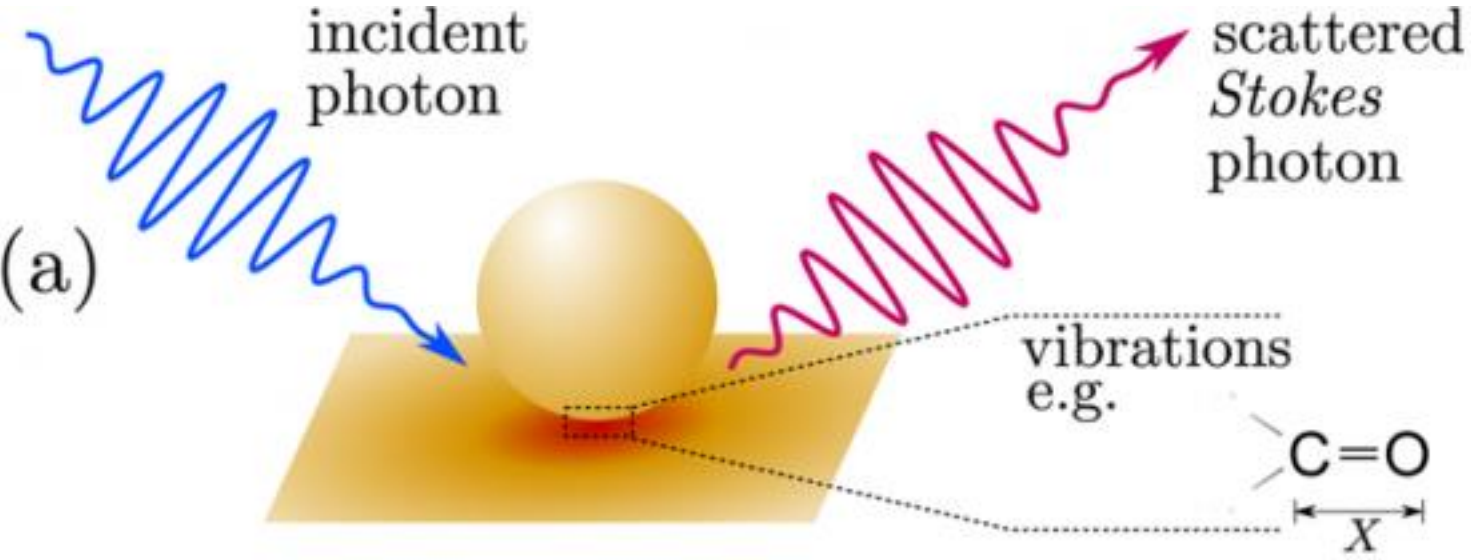
Raman spectra= fingerprint of materials

10^7 incident photon→ only 1 photon is Raman scattered → low intensity → need to be enhanced

Surfaced enhanced Raman scattering

- Scattering process

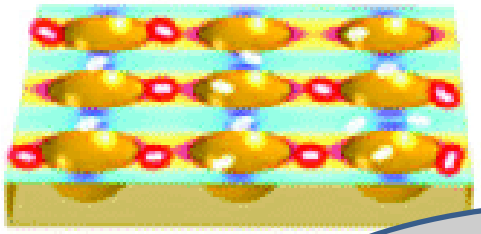




1. Introduction
1.2. SERS effect

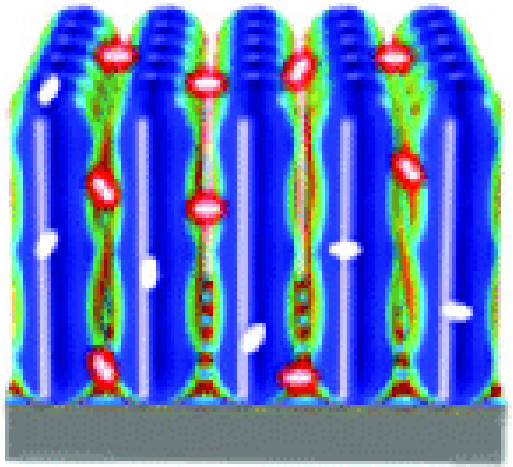
Traditional SERS substrates ⇔ rough surface or metal nanoparticles like Au, Ag, Cu,…

High randomness ; low repeatability; low stability, impossible for qualification study …



SERS substrates from aligned-stable nanowires grown on solid material

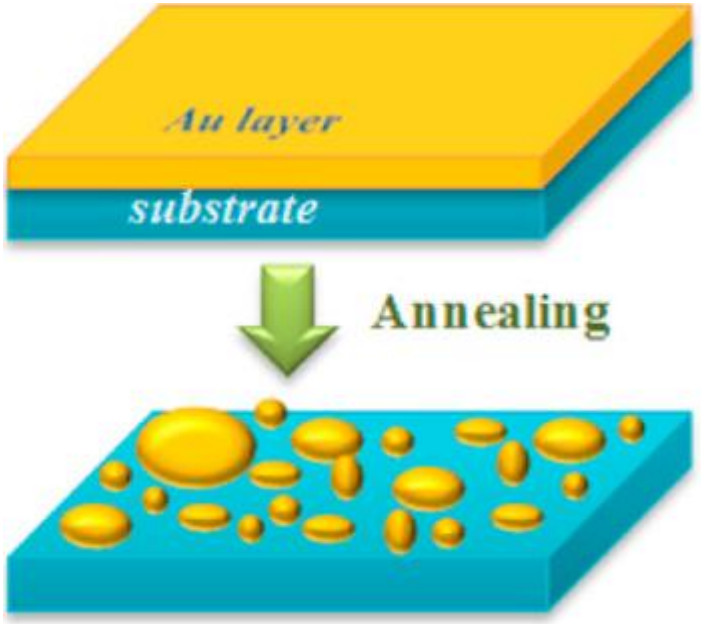
ZnO/CuO 1D nanostructures coated with Au/Ag



Au nanostructures fabrication

Au nanostructures

1. Cleaned lamen substrates
2. Sputtering of Au (20 mA; 10 → 70 s)
3. Annealed at 300°C in 2h.



ZnO/Au nanowires fabrication

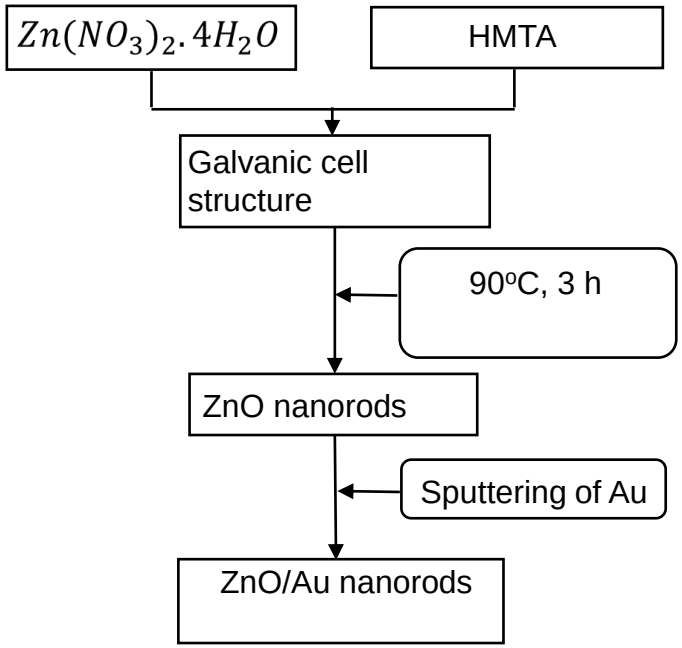
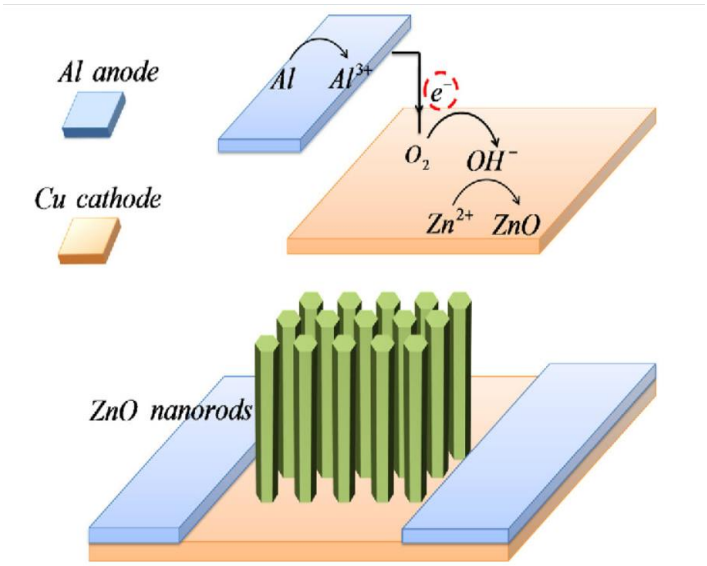


Diagram of ZnO/Au fabrication process

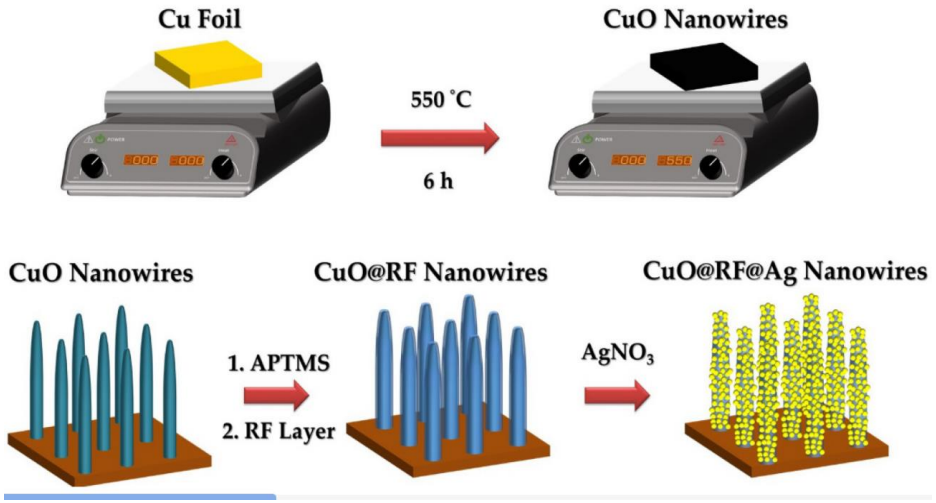


Growth mechanism of ZnO nanorods by hydrothermal assisted with galvanic effect

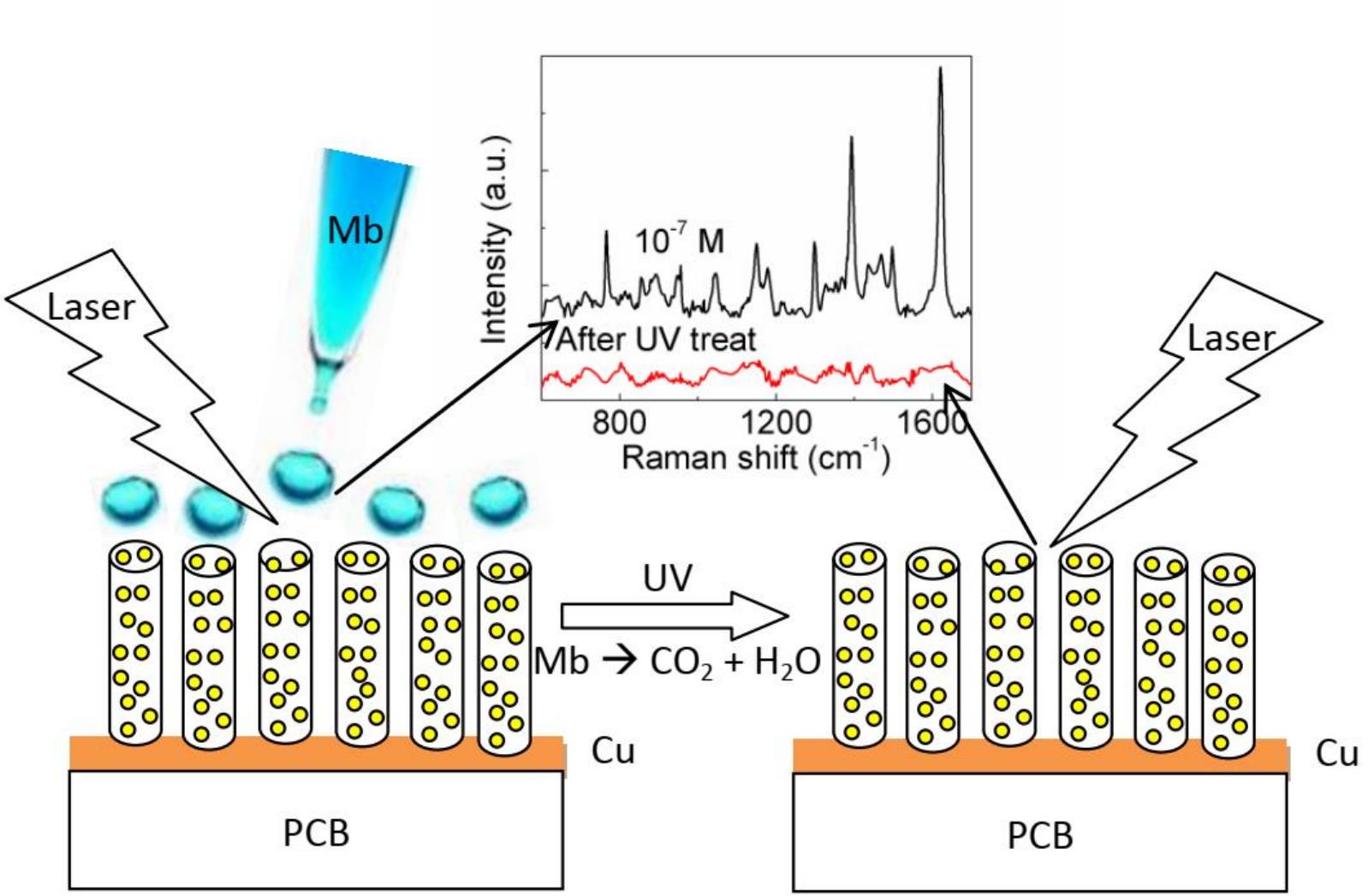
CuO/Au nanowires fabrication

Nano CuO/Au

1. Cleaning Cu substrates with DI water, ethanol, aceton and HCl
2. Annealing at 500°C in 2h.
3. Sputtering of Au on the asprepared CuO nanowires (20 mA, 80 s → 640 s)

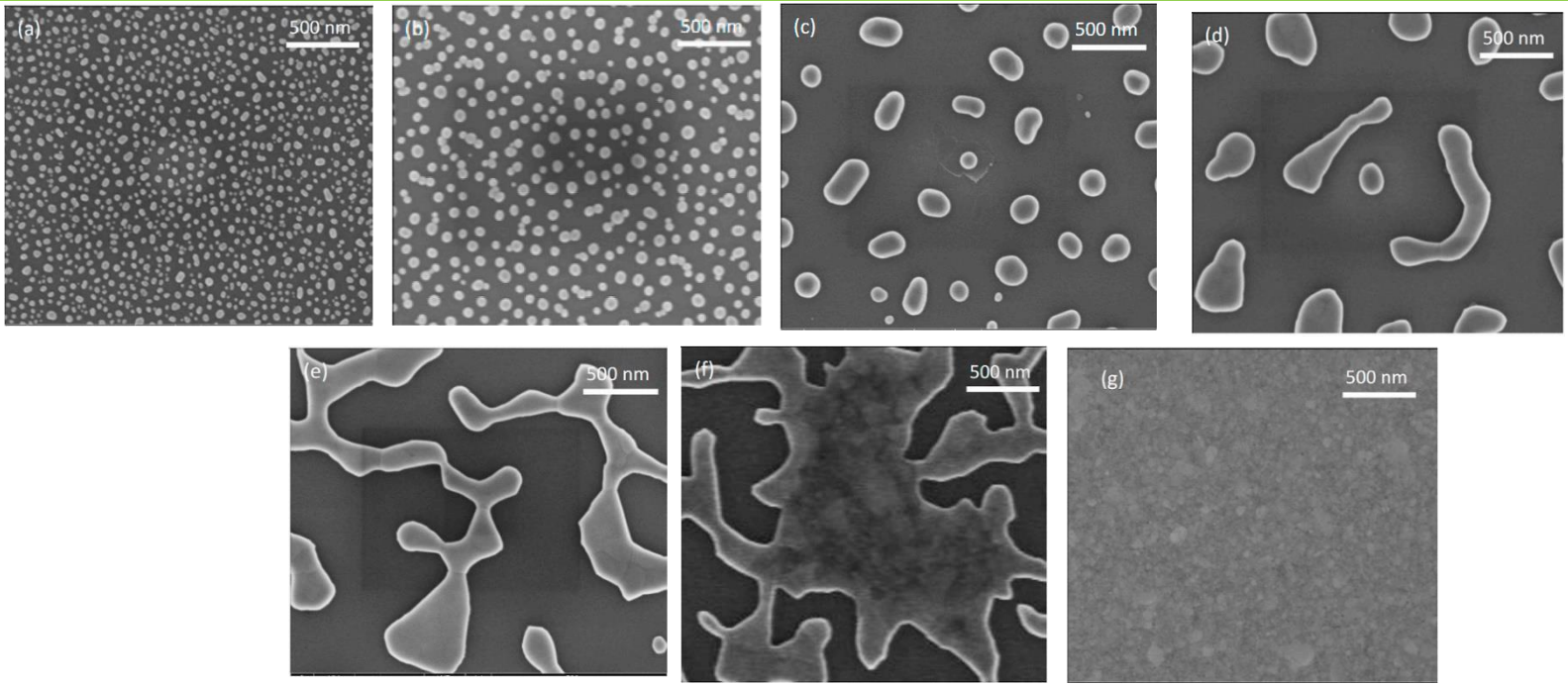


SERS measurement setup



Results and Discussion

SERS substrates based on Au nanostructures



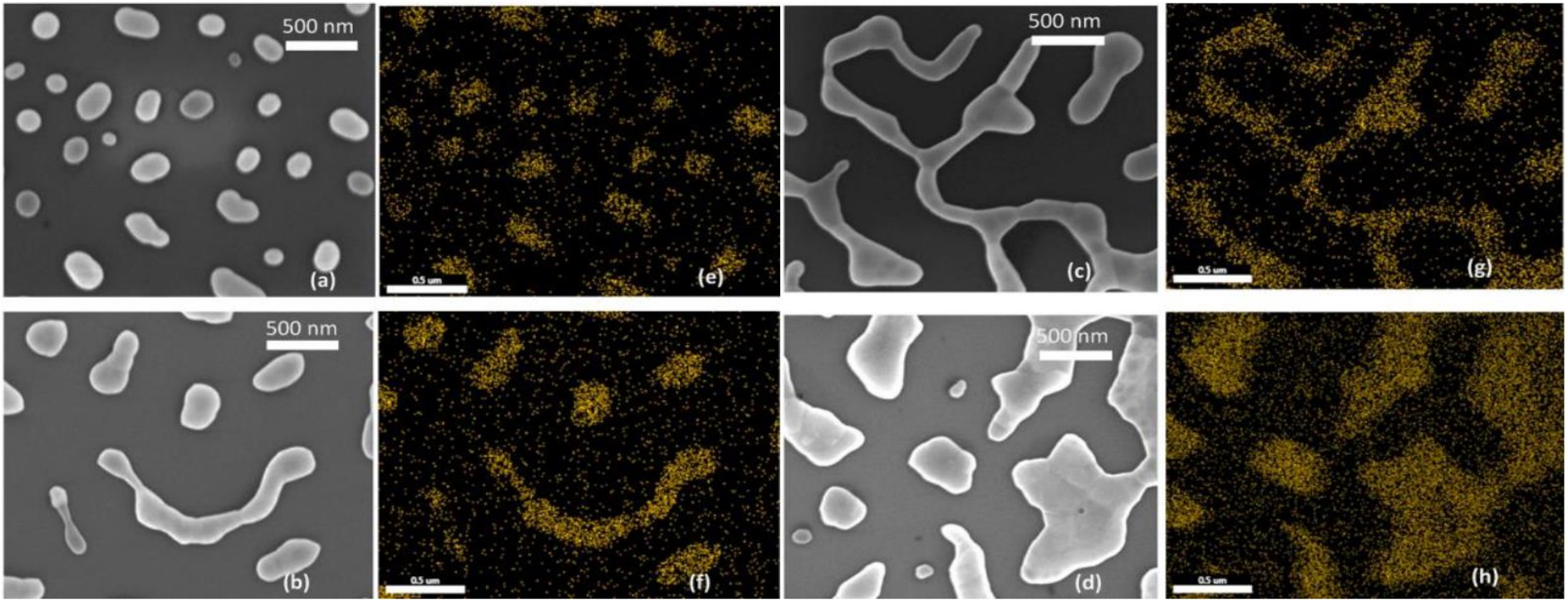
SEM images of Au nanostructures prepared with different sputtering times from 10 s to 70s (a→g) and heat treatment at 300 °C.

Increasing annealing time → particle size increases accordingly.

t> 40 s → complexed morphology

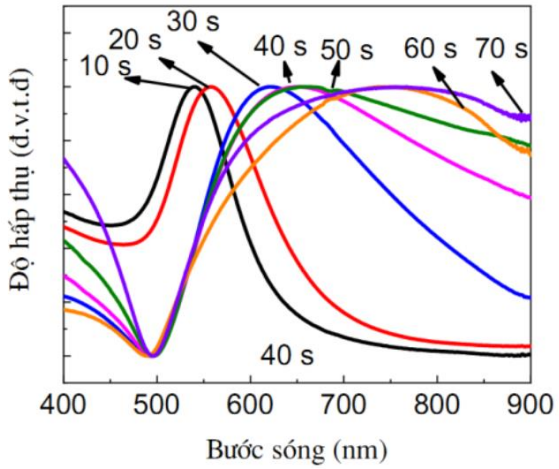
t> 70 s → continuous films

SERS substrates based on Au nanostructures

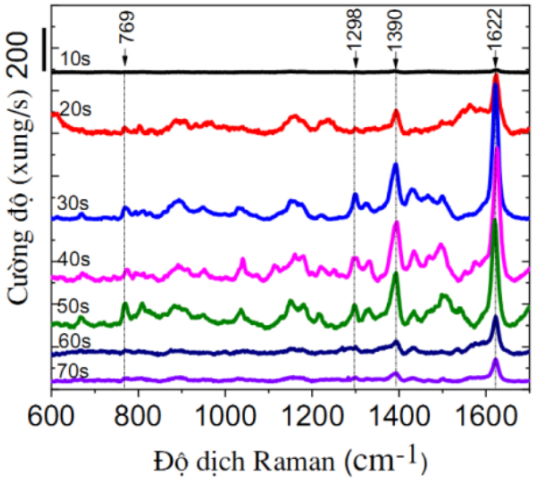


SEM images and EDS mapping images (tracing Au signal) of samples prepared with different sputtering times 30s (a, e), 40 s (b, f), 50 s (c,g) , 60 s (d,h)

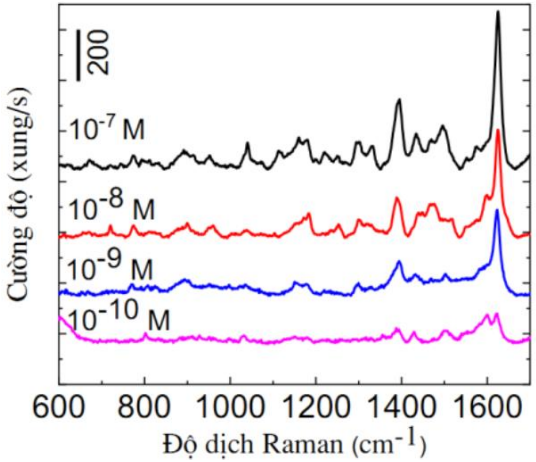
SERS substrates based on Au nanostructures



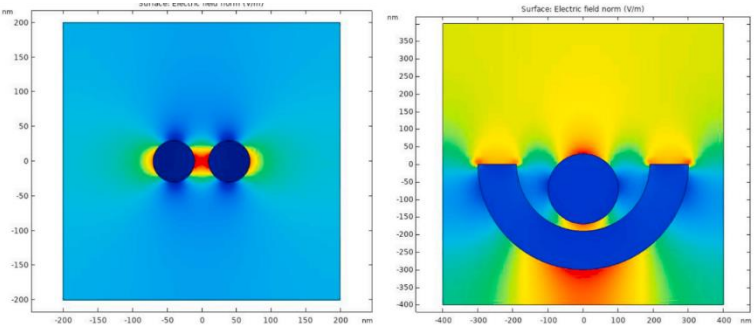
Absorption spectra of Au nanostructures prepared with different sputtering time: from 10 s to 70 s.



Raman spectra of MB (10^{-7} M) measured on gold nanostructures preapared with different sputtering times:



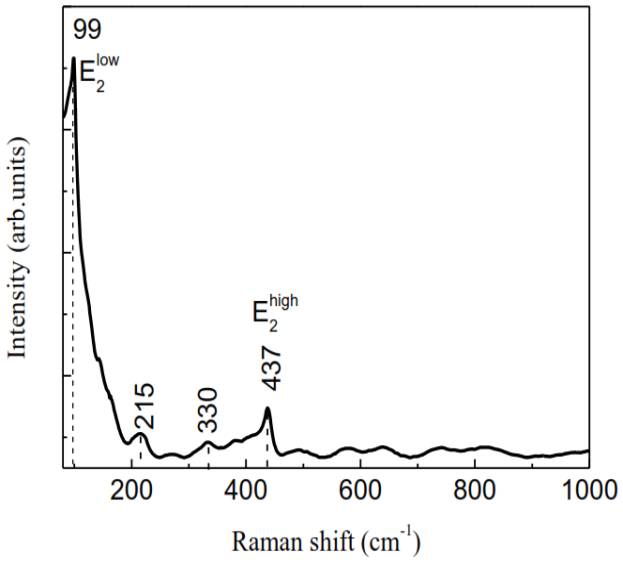
Raman spectra of MB of different concentrations measured on gold nanostructures prepared with sputtering time of 40 s.



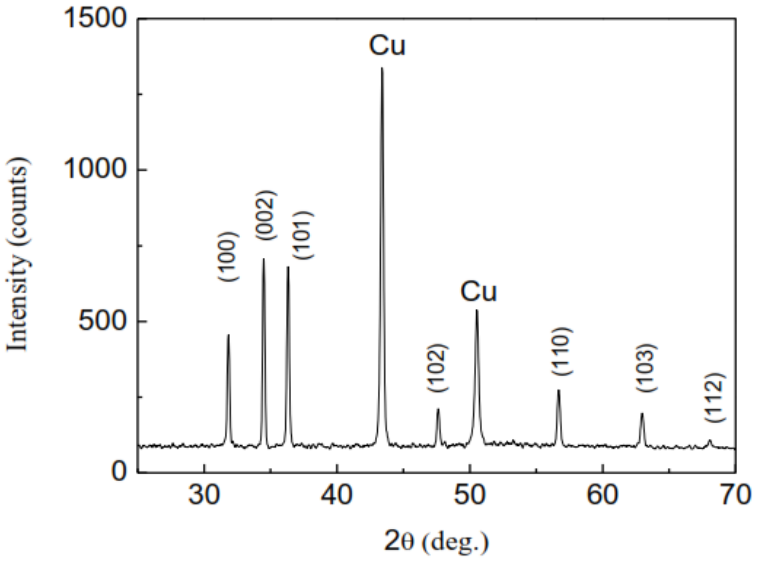
Simulation of electro magnetic field distribution generated by Au nanoparticles and Au complex nanostructures

**T.H. Tran, V.T. Nguyen et al., Optical Materials 121 (2021) 111488*

SERS substrates based on ZnO/Au nanorods

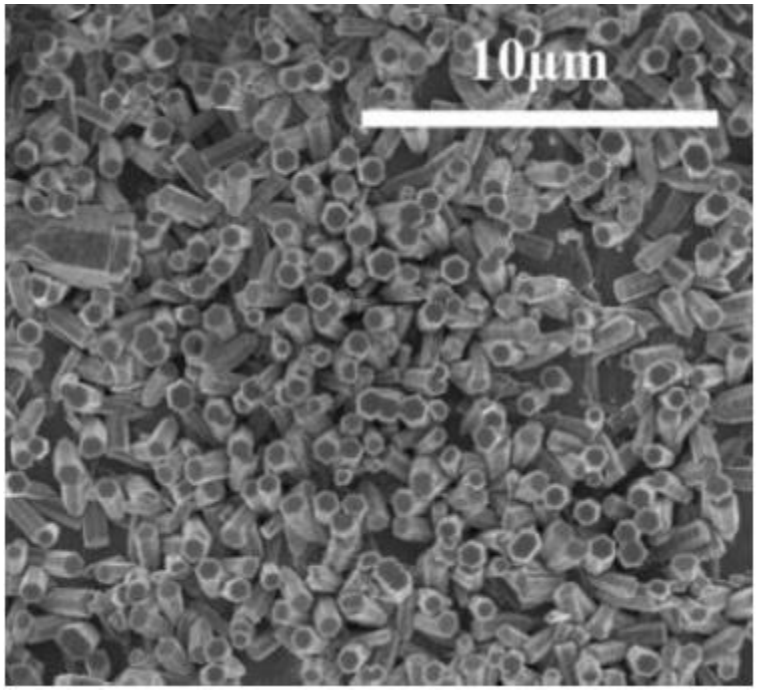


Raman spectra of ZnO samples prepared by galvanic effect assisted hydrothermal method.

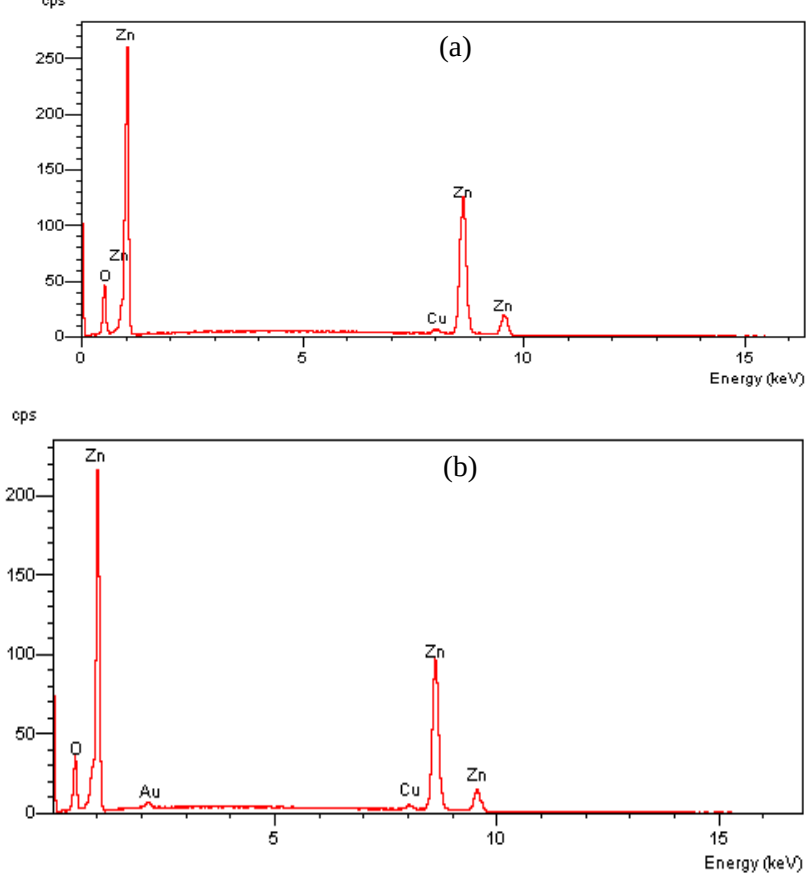


XRD patterns of ZnO nanorods prepared in 3h at 90 °C.

- The as-prepared product is single phase of good crystal quality

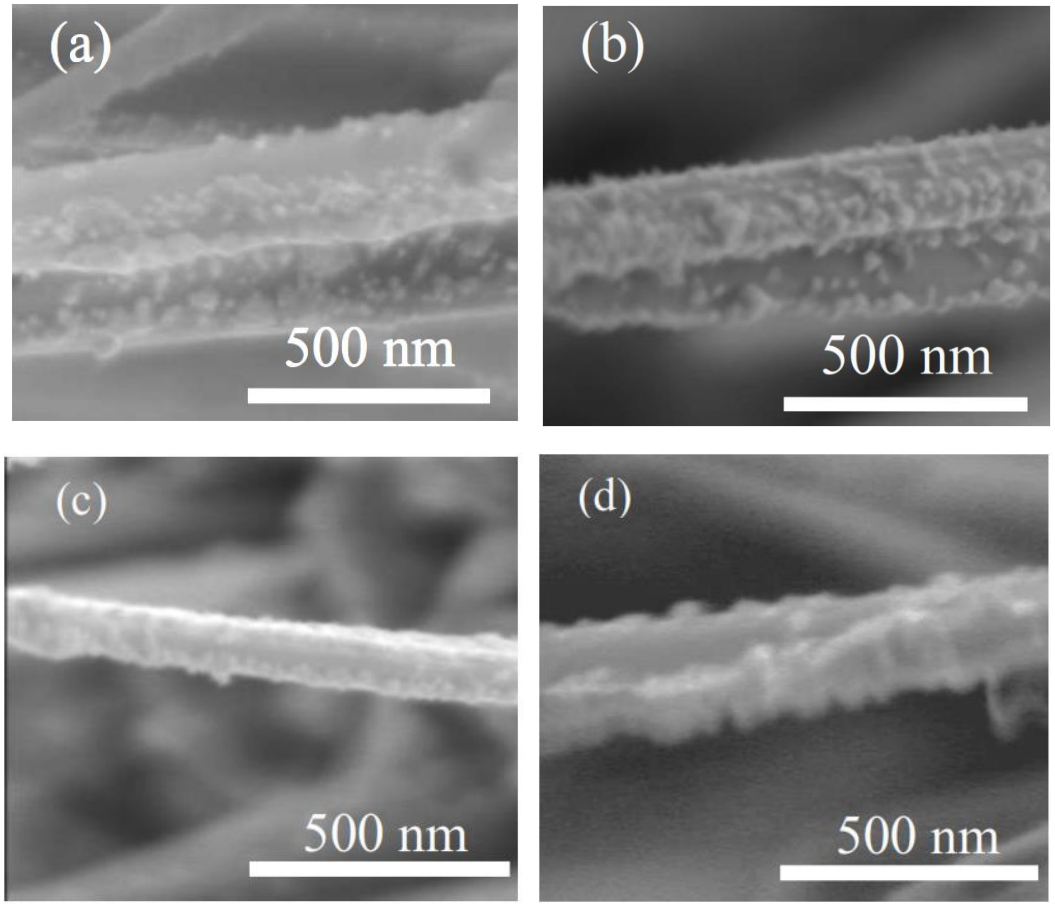


SEM images of the as prepared ZnO nanorods.

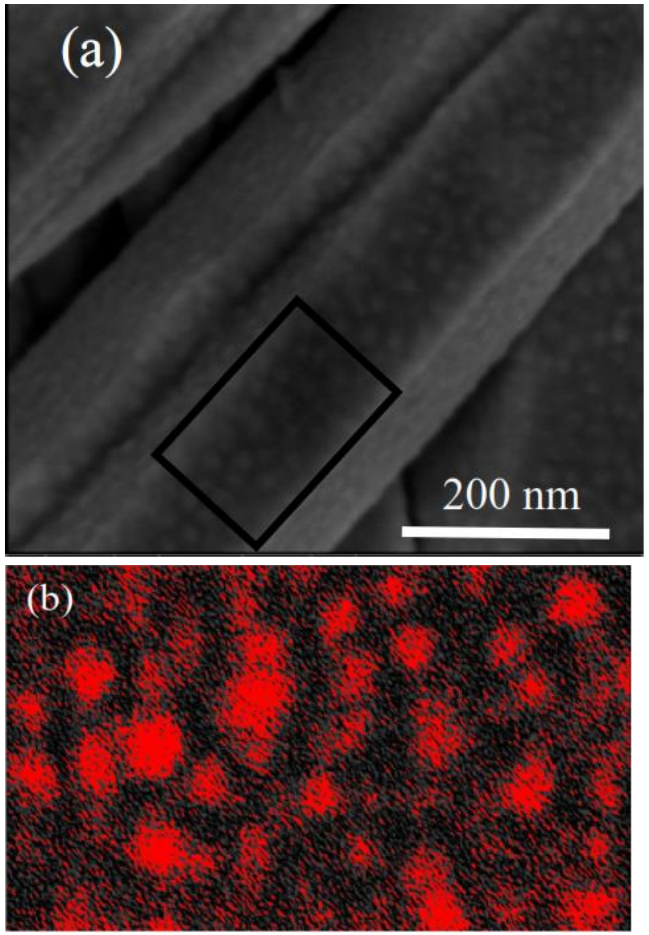


X-ray energy dispersive spectra of ZnO nanorods prepared in 3h and ZnO@Au nanorods with sputtering time of 10 s.

- Nanorods are of high density, uniform, have good alignment.
- The samples is pure
- After sputtering, clear trace of gold was observed.



SEM images of ZnO nanorods decorated with gold at different sputtering time: (a) 10s; (b) 30s; (c) 60 s and (d) 120s.



(a) Enlarged TEM image of ZnO@Au nanocomposite sample prepared with sputtering time of 30s and (b) EDS mapping of Au element on the surface of ZnO nanorods

- Sputtering time
- less than 30 s → gold nanoparticles
- Over 30s → layer (core/shell structure)

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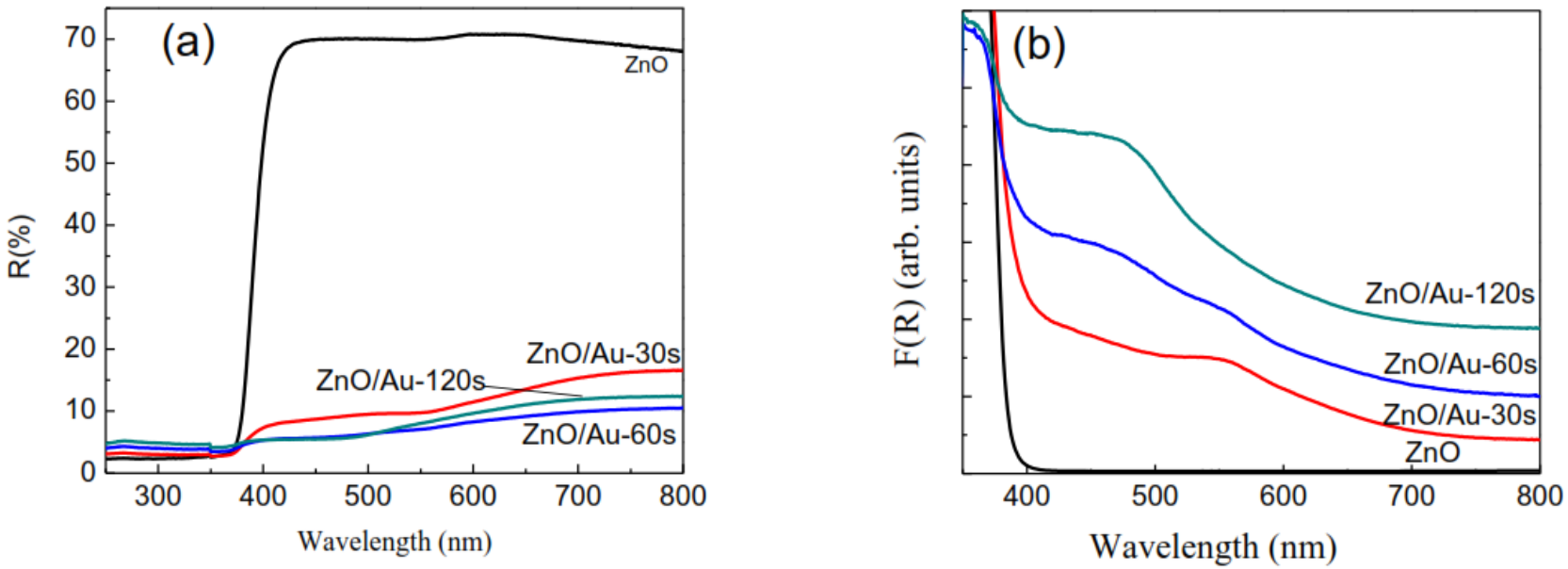

Diffuse reflectance spectra of ZnO and ZnO@Au nanorods with different sputtering time, b) the corresponding absorption spectra of ZnO and ZnO@Au nanorods with different sputtering time.

- Surface plasmon resonant peak observed for sample sputtered in 30s.

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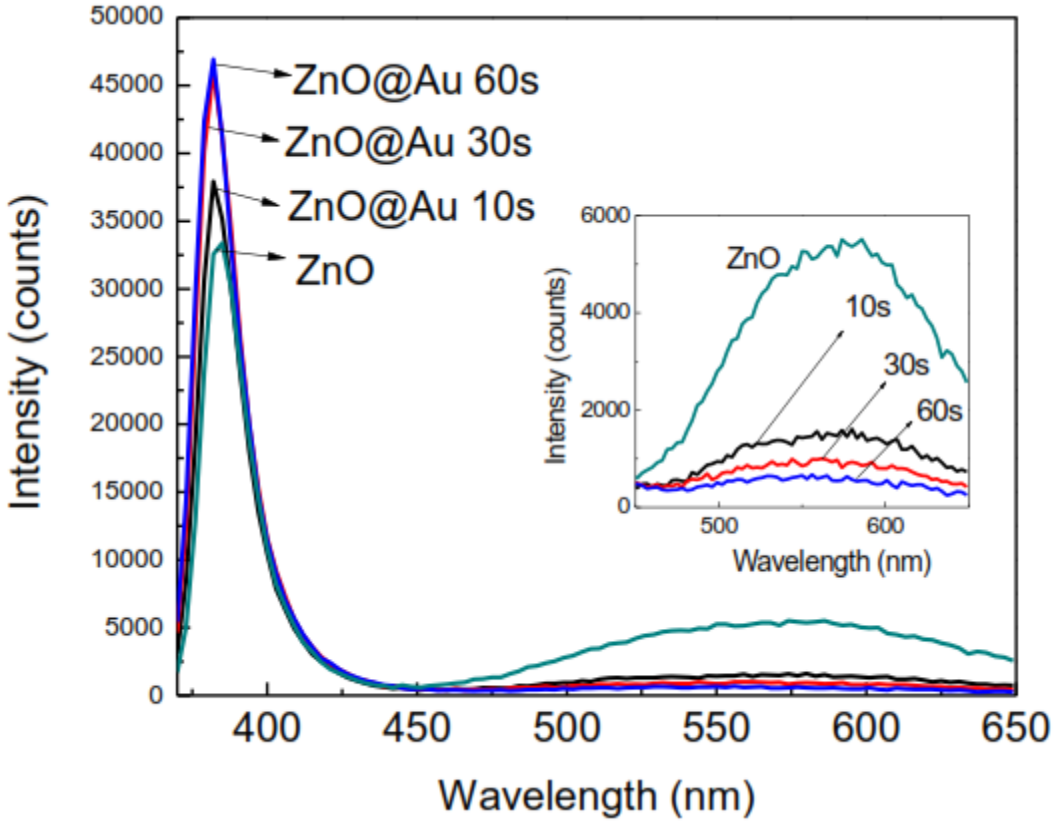

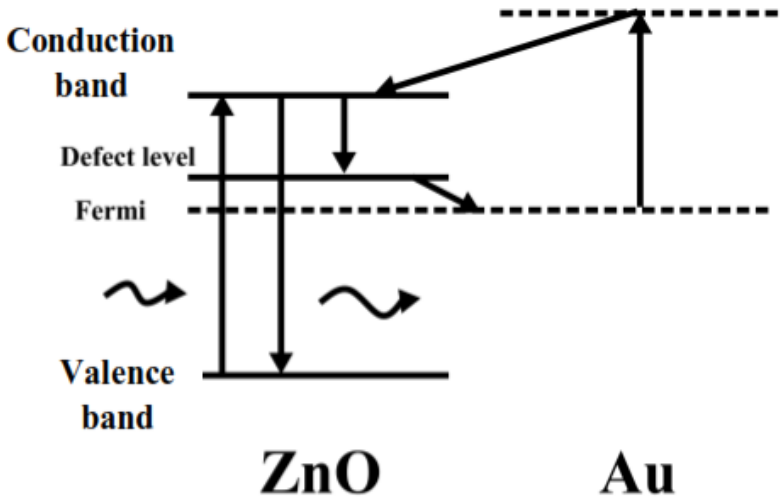

Photoluminescence of ZnO@Au nanorods prepared with different sputtering time.

- Band to band transition is enhanced.

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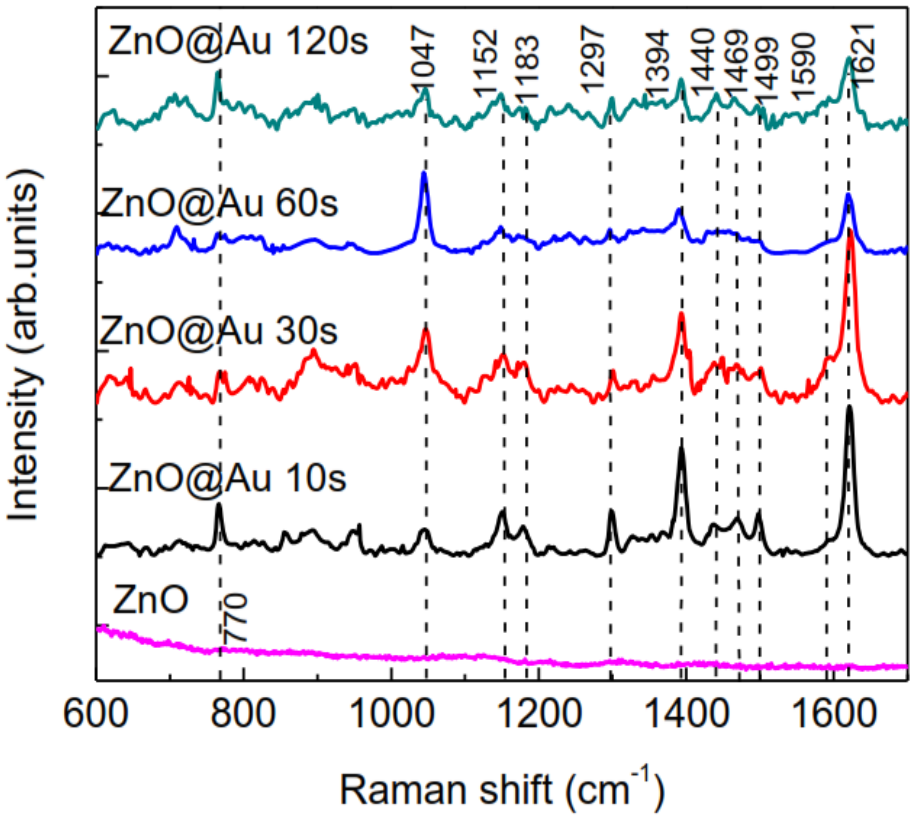
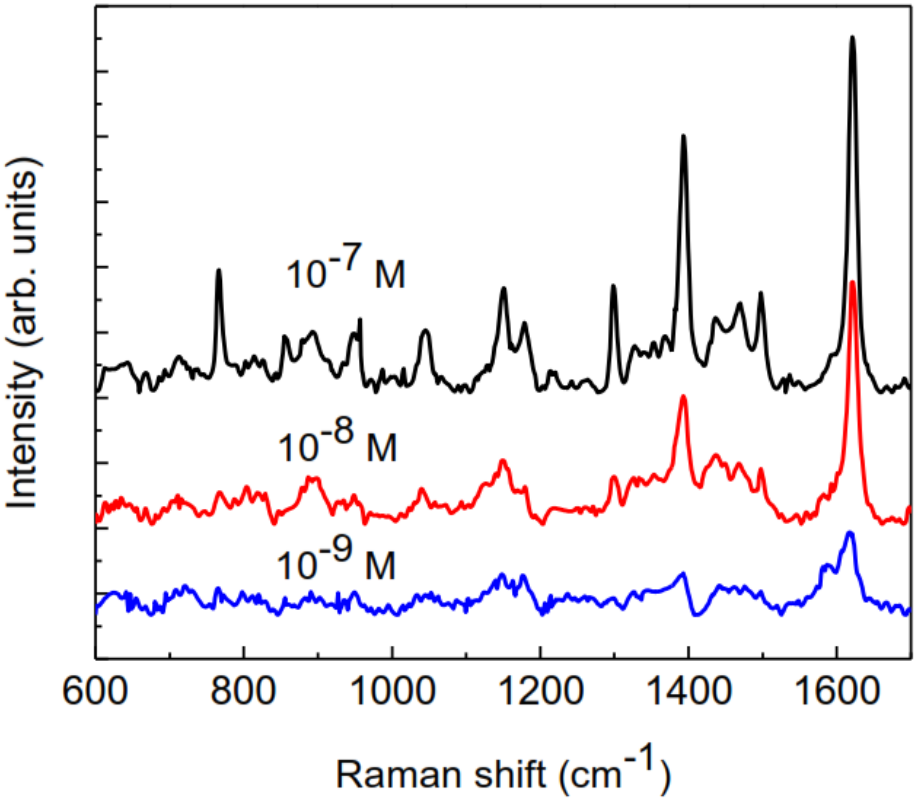


Raman spectra of MB (10^{-7}M) on ZnO@Au nanorods prepared with different sputtering time.



Raman spectra of MB at different concentration measured on ZnO/Au with sputtering time of 30s.

- Raman enhancement Is strongly depended on sputtering time.
- 30s → highest enhancement
- Limit of detection ~ 10^{-9} M

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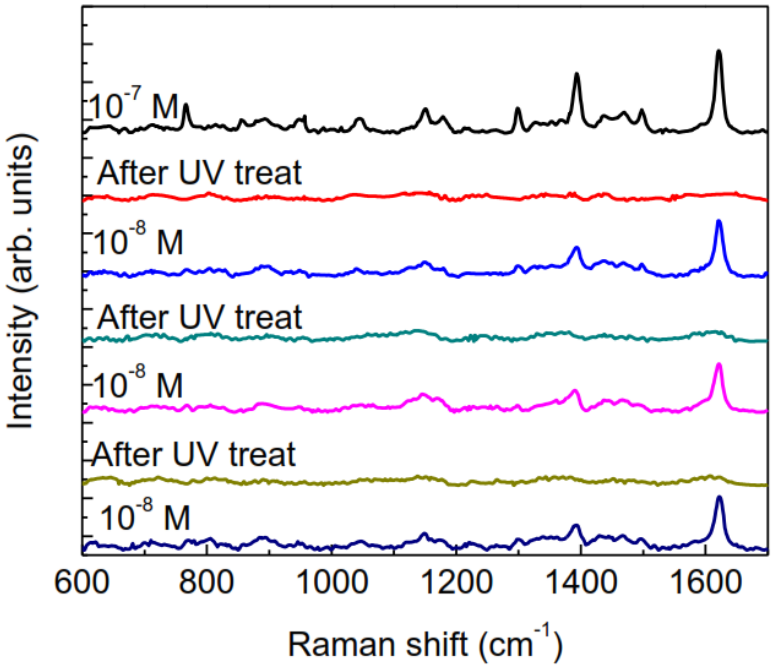

Raman spectra of MB on ZnO@Au nanorods during adsorption/cleaning cycles.

- As-prepared SERS substrate is recyclable

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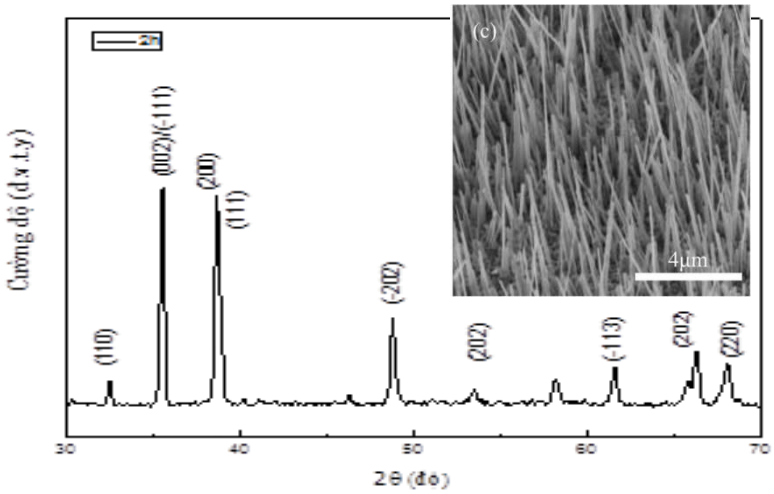
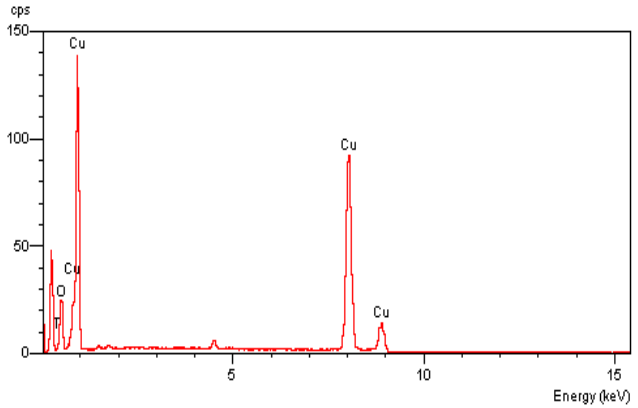
SERS substrates based on CuO/Au nanowires

- **Characteristics of CuO nanowires**



XRD diffraction pattern and SEM image of CuO nanowires



EDS spectrum of CuO nanowires

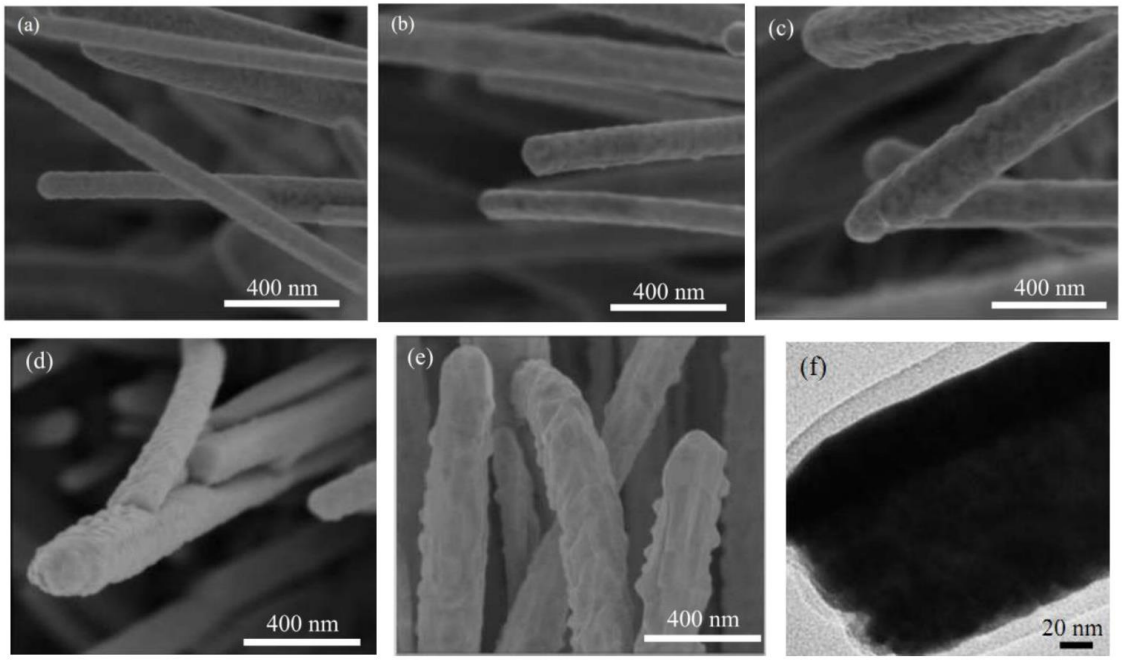
✓ The product is pure and of high crystal quality as shown by XRD pattern and Eds spectrum.

→ The obtained products are CuO nanowires of high density and preffered orientation.

SERS substrates based on CuO/Au nanowires

- **Characteristics of CuO nanowires**

- Au shell thickness increases accordingly with sputtering time.
- Au shell thickness plays an importance role on Raman enhancement capability.



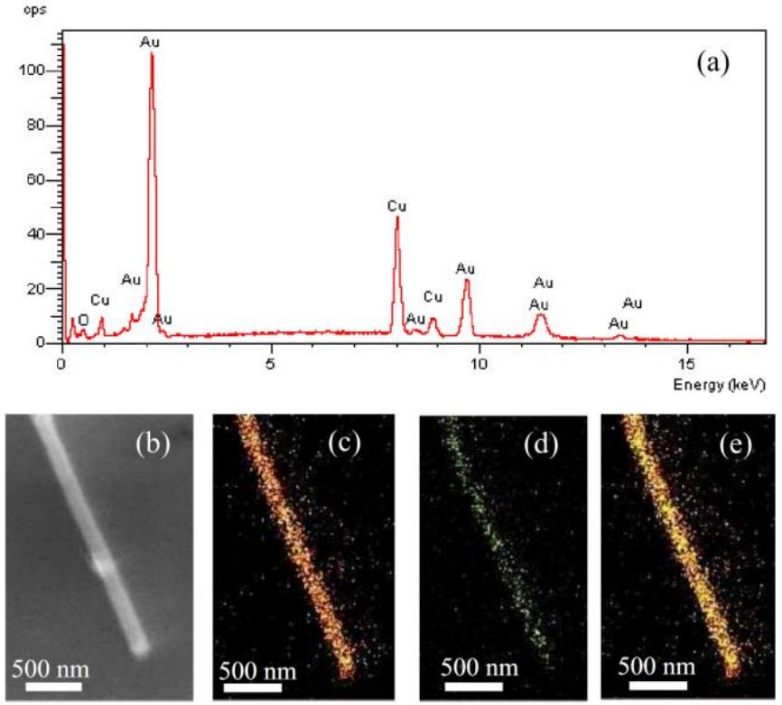
SEM images of CuO/Au nanowires preapared with different sputtering time: a) 80 s b) 160 s, c) 320 s, d) 480 s; e) 640 s and f) HRTEM image of a CuO/Au nanowire

SERS substrates based on CuO/Au nanowires

- **Characteristics of CuO nanowires**

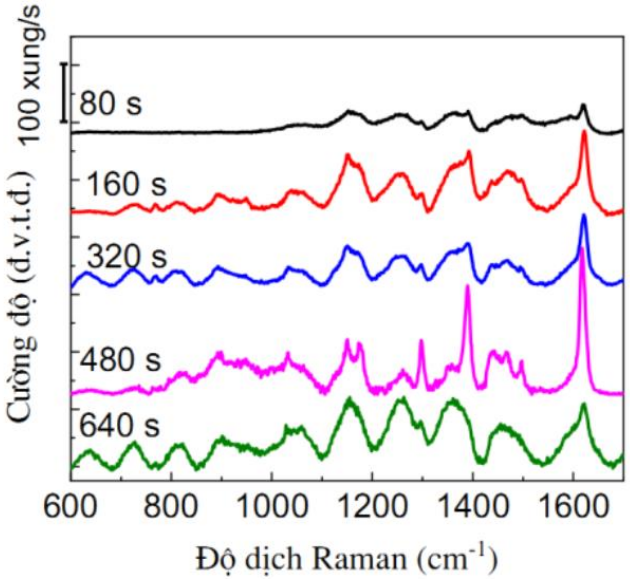
✓ Existence of Au on CuO nanowires is confirmed by clear EDS signal.

✓ Mapping shows that Au is distributed evenly on CuO nanowires, in agreement with HRTEM image.

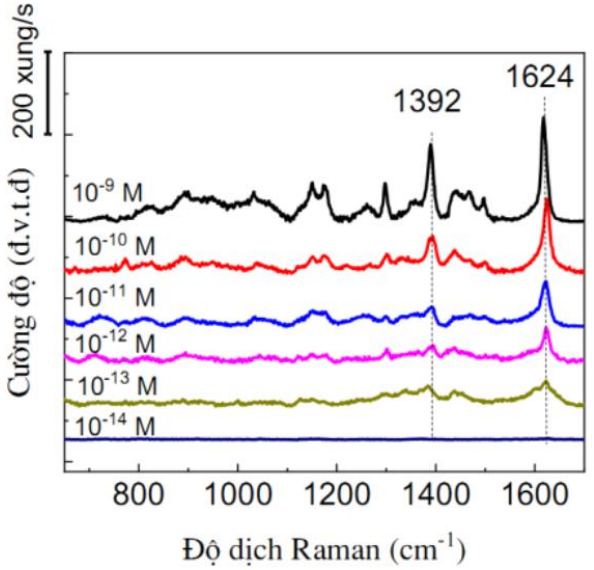


EDS spectrum of CuO/Au nanowires prepared with sputtering time of 80s (a); element mapping images by EDS of (c) Au, (d) Cu và (e) accumulation of Cu, Au.

Raman enhancement on CuO/Au nanowires**



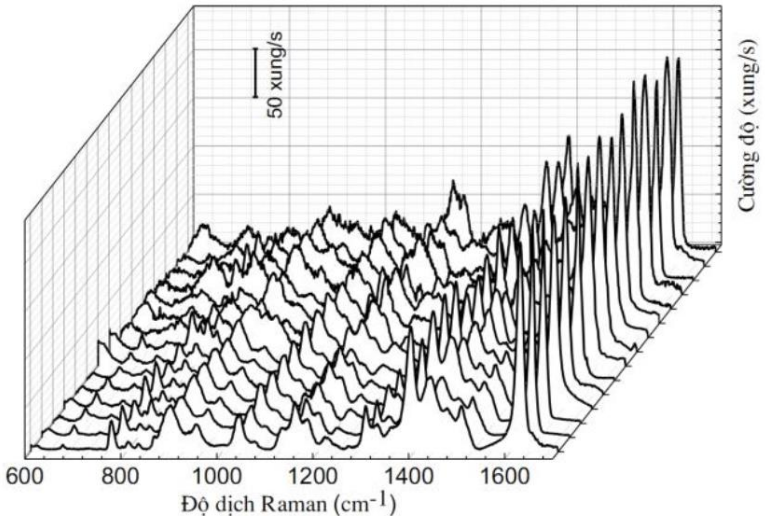
Raman spectra of MB 10^{-9} M measured on CuO/Au nanowires prepared with different sputtering times.



Raman spectra of MB at different concentration measured on CuO/Au nanowires prepared with different sputtering time of 480 s.

**T. H. Tran, Ceramics International, https://doi.org/10.1016/j.ceramint.2021.10.093

Raman enhancement on CuO/Au nanowires



SERS spectra of MB 10^{-10}M measured at 15 random points on CuO/Au nanowires.

No.	Group	Materials	LoD
1	G. Sinha [6]	ZnO/Au	10^{-12} M
2	Pangpaiboon [9]	ZnO/Au	10^{-7} M
3	This research	CuO/Au	10^{-13} M

**T. H. Tran, Ceramics International, https://doi.org/10.1016/j.ceramint.2021.10.093

4. Conclusions

We successfully fabricated Au nanostructures; ZnO/Au nanorods and CuO/Au nanowires as SERS substrates with high repeatability and sensitivity.

Simultaneous enhancement of optical properties offers a kind of ZnO/Au SERS substrate of high enhancement factor, high uniformity, with self cleaning effect.

SERS substrates based on CuO/Au nanowires are highly sensitive, that can detect Methylene Blue at ultralow concentration (~10^{-13}M)

Future work

- Detection of phenol at low concentration (< 10^{-6} g/L) in water for quality control of civilian water supply.
- The study is currently expanding on measuring glucose at sub-physiological range by SERS, which can hopefully be used to diagnostic diabetes via testing glucose level in saliva.

Group members

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Dr. Quang Hoa Nguyen

Dr. Cong Doanh Sai

Dr. Thi Ha Tran

- Thank you for your attention!