

Introduction

We studied the non-resonant SERS activity of a standing arrays zinc oxide/gold encapsulated in silica shell. This semiconductor/nobel metal hybrid materials gives a strong and reproducible Raman signals in the near-infrared region; which leads to a significant reduction in fluorescence interference and sample photodegradation. The fabricated substrate is then applied for quantifying the composition of xylene isomers in xylene histological grade sample. The result exhibits 4% error compared to gas chromatography and the limit of detection is 14 ppm for o,m-xylene and 35 ppm for p-xylene.

Qualitative techniques for xylene detection



- Portable device, NIR laser suitable for biosamples
- Fast and non destructive detection
- Does not require extensive sample preparation
- Economic way to quantify all three isomers of xylene



- Complex instrumentation
- General column cannot separate p,m-xylene
- Specific column for p,m-xylene is \$ 3,000
- Require sample dilution

- Other analytical techniques include: solid phase microextraction with spontaneous Raman spectroscopy¹ or mid-infrared evanescent filed spectroscopy² can have lower detection limit but require rigorous sample preparation and heavy instrumentation.

Characterization

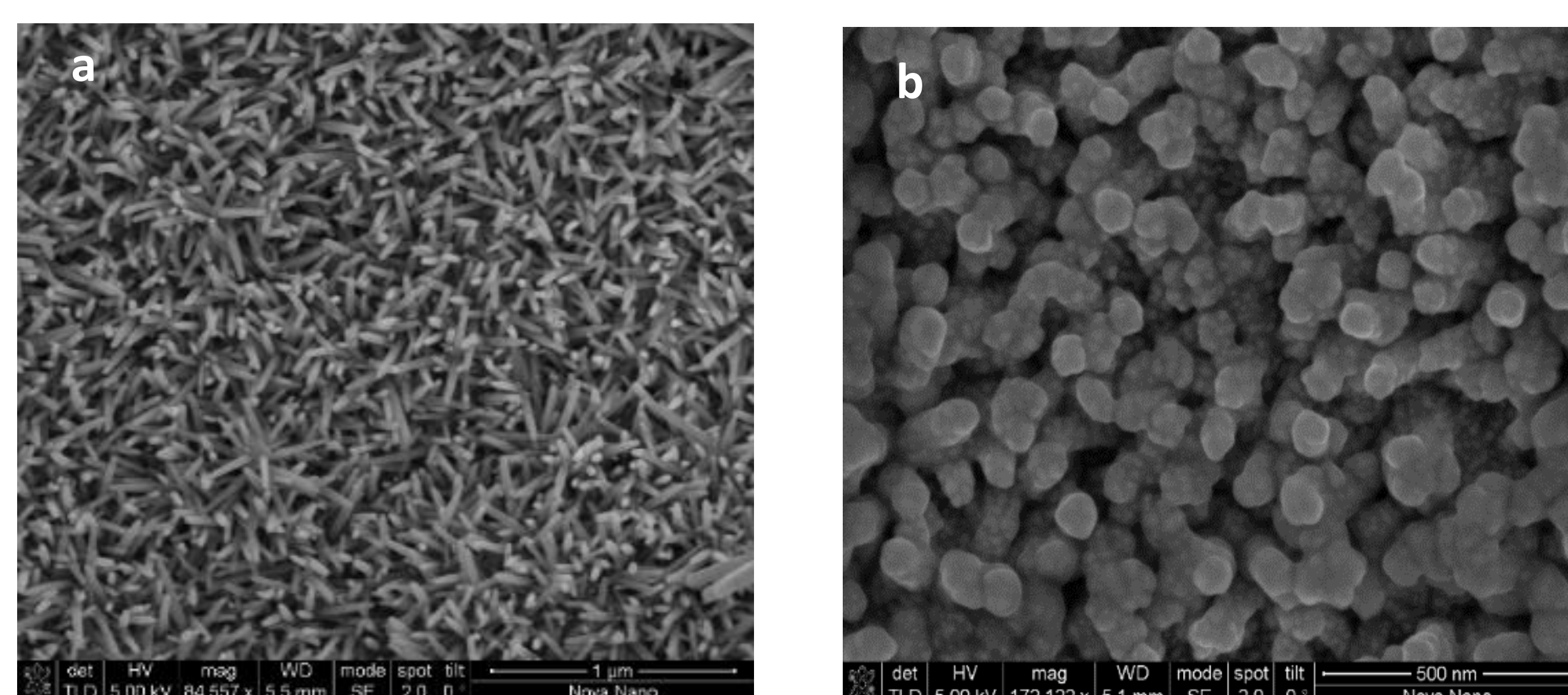


Figure 1. (a) SEM images show changing of morphology after growing ZnO nanorod forest on gold coated glass, (b) treated with gold salt showing the formation of gold nucleation sites

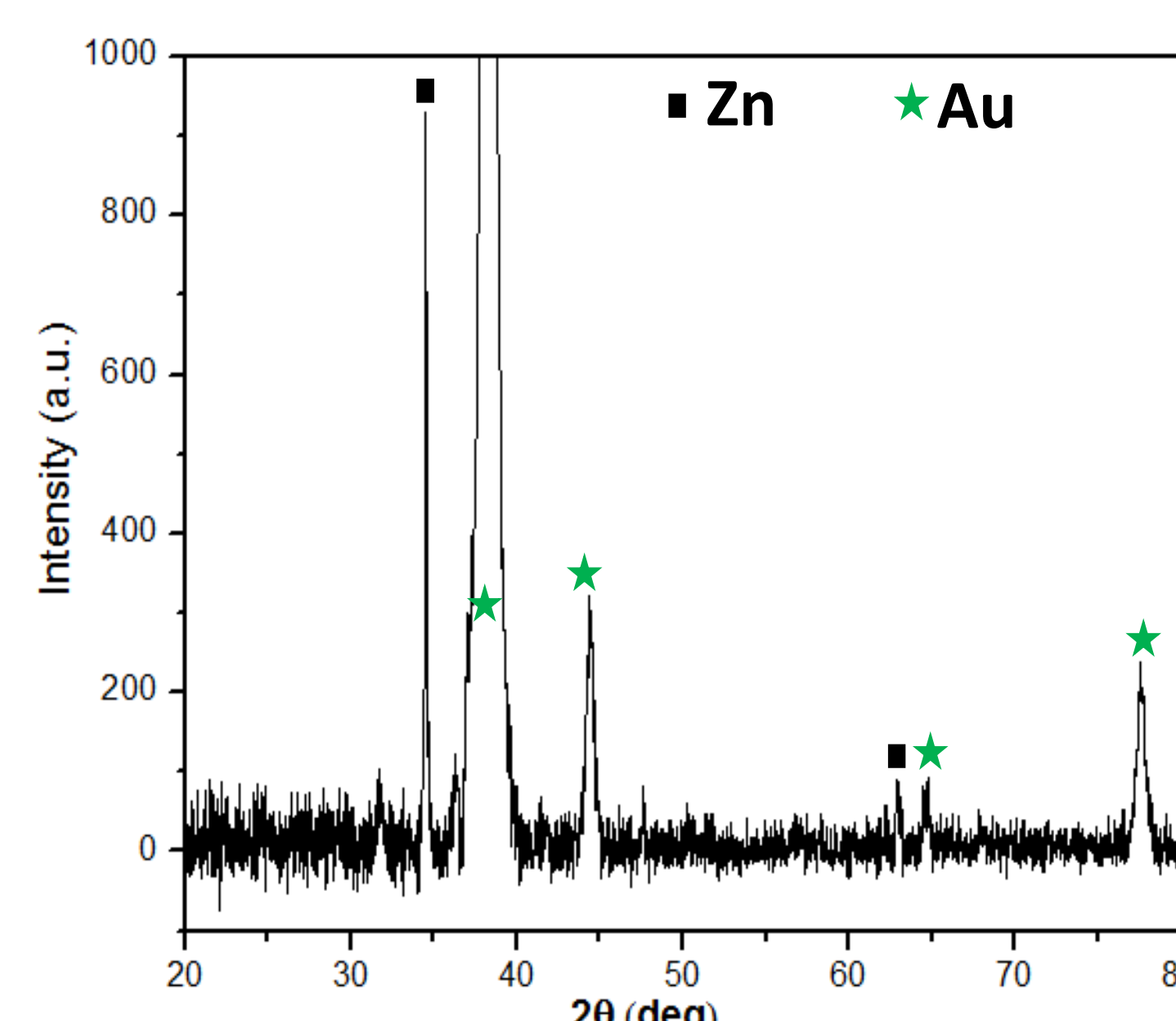


Figure 2. XRD analysis of gold seed formation on ZnO nanorods forest

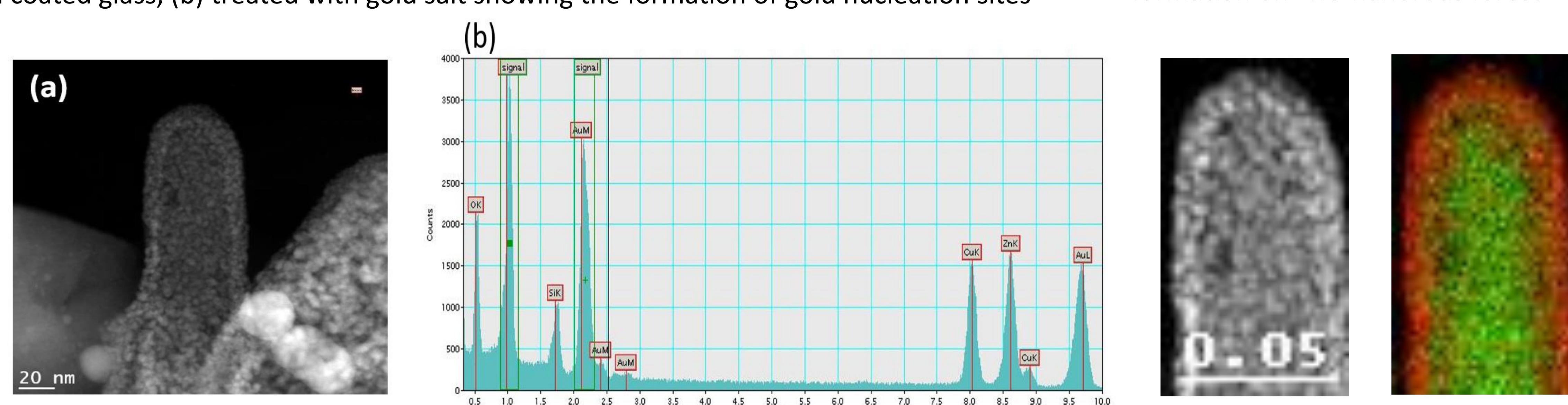


Figure 3: (a) TEM image of single ZnO rod from substrate, (b) elemental profile of the feature for mapping.

Xylene isomers detection and quantification

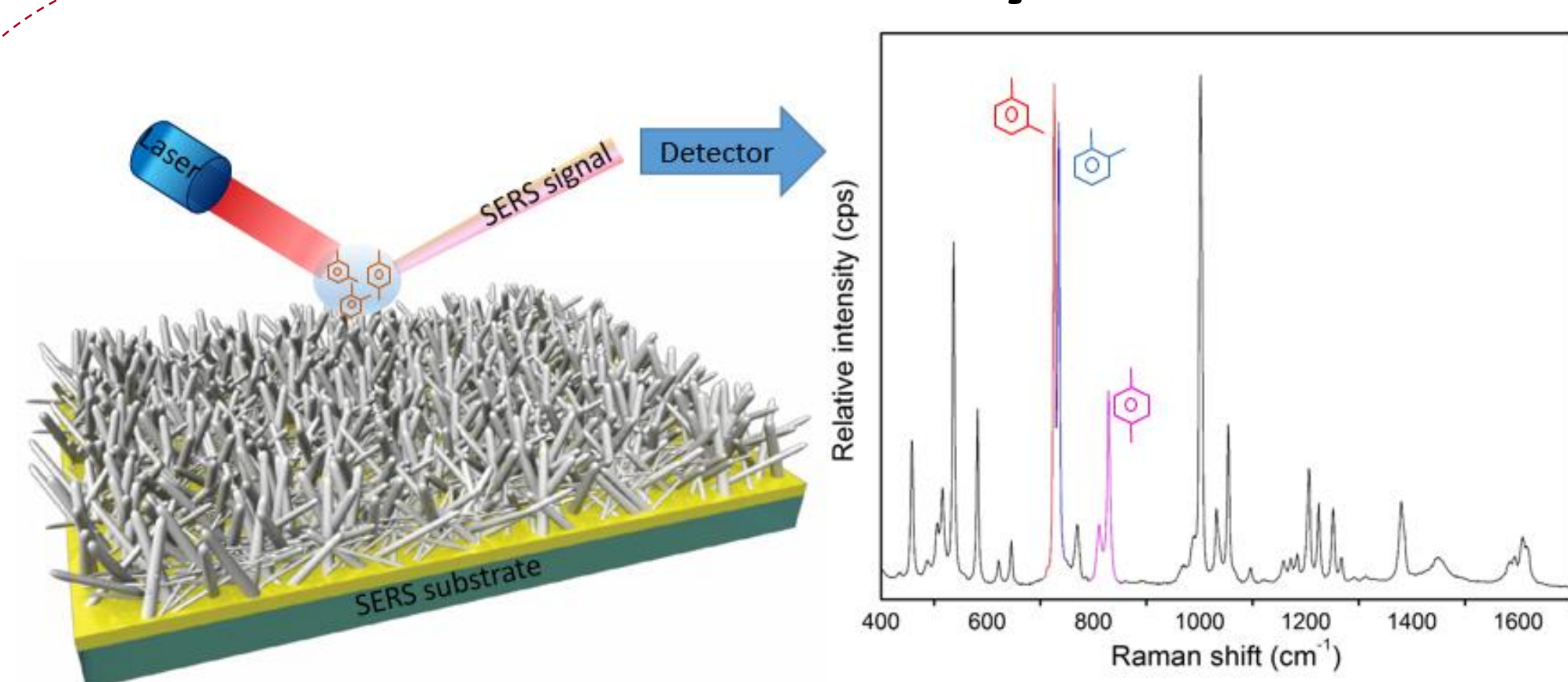


Table 1. Comparative xylene composition from calibration data and GC

	%difference
p-xylene	3.7
m-xylene	3.7
o-xylene	2.9

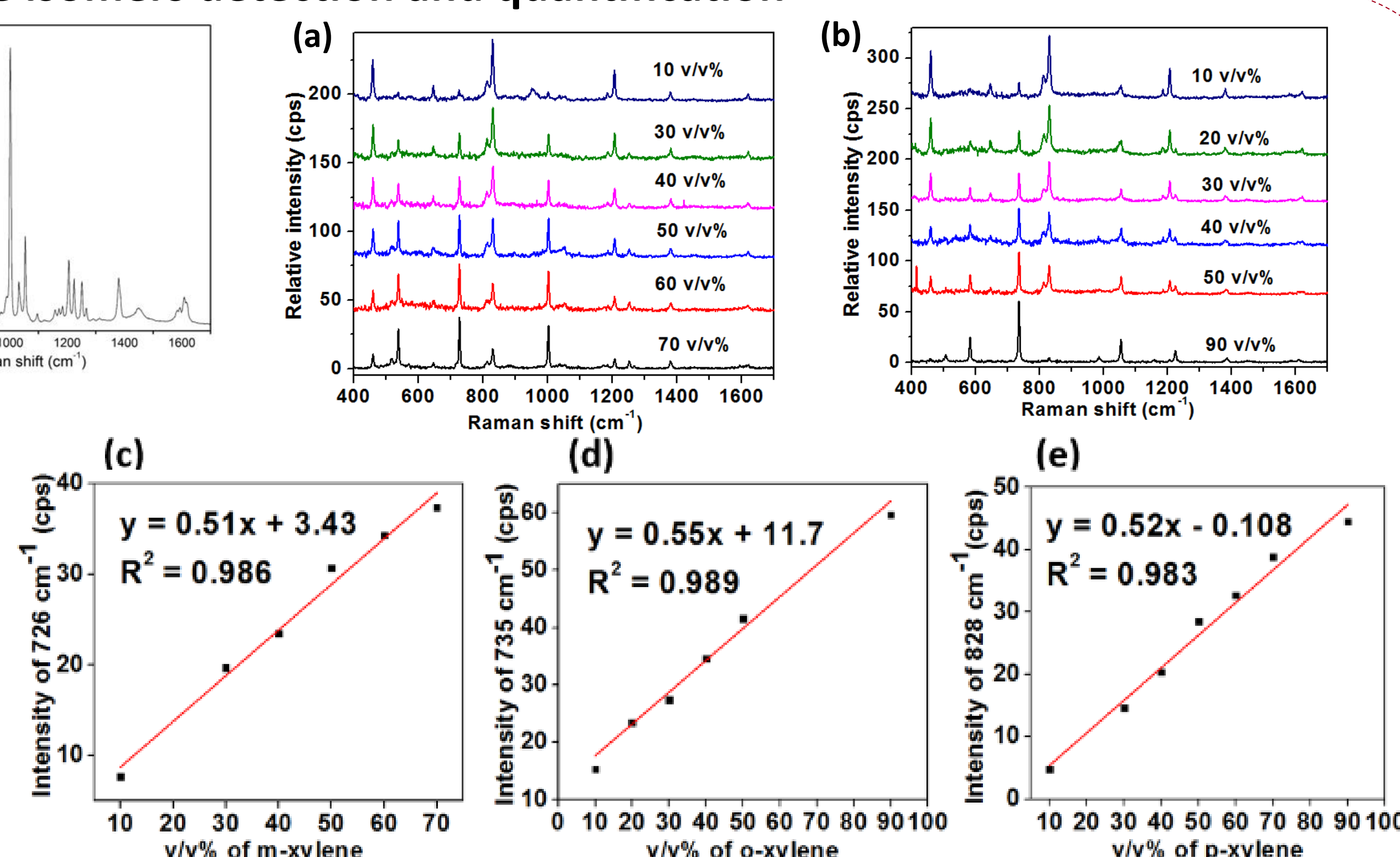
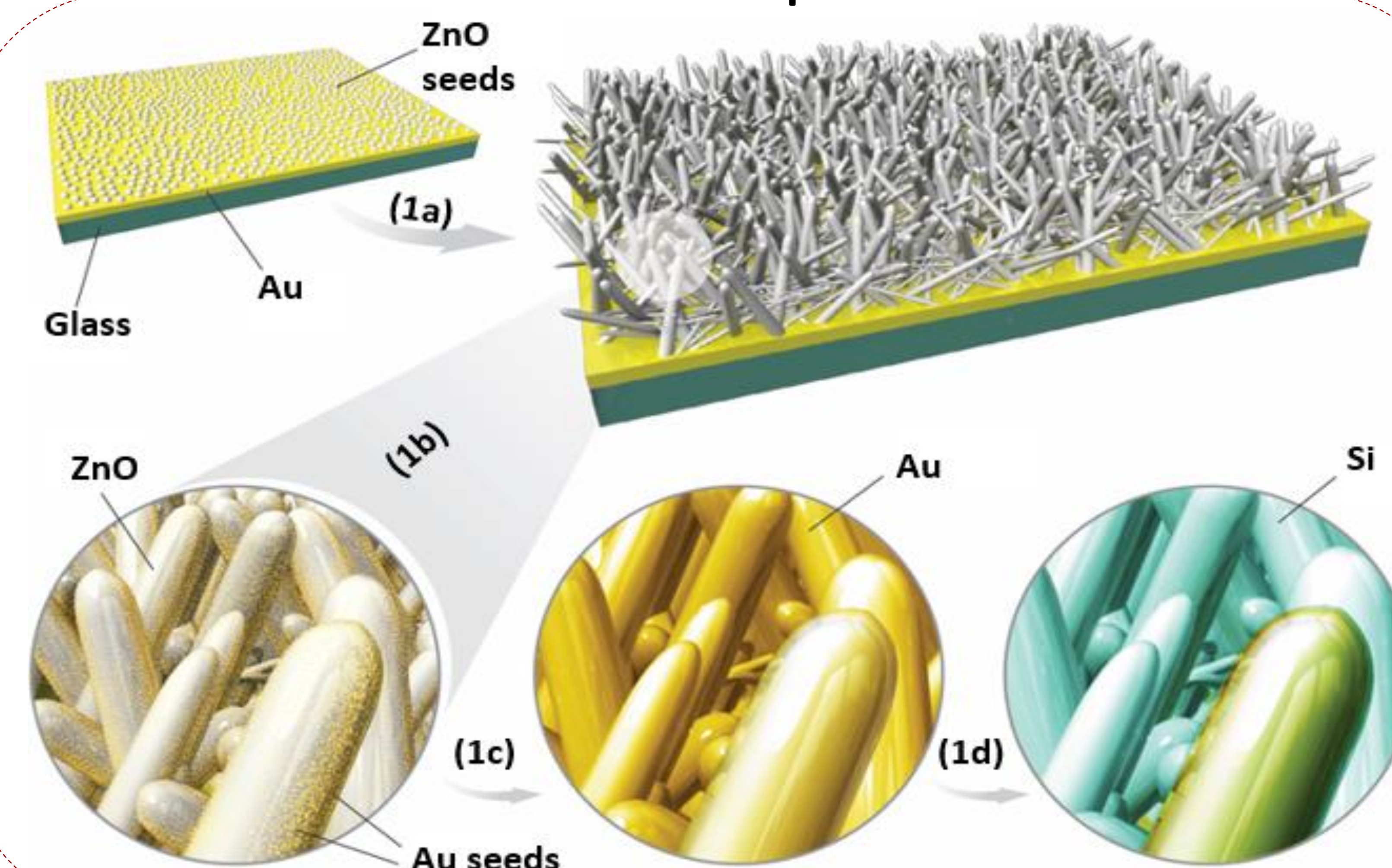


Figure 4. SERS of (a) m-xylene and (b) o-xylene with different v/v% with p-xylene, (c,d,e) Calibration data of intensity at characteristic peak versus v/v% of each isomer

Fabrication process



Experimental results

- Enhancement factor 2×10^4 for 4-mercaptobenzoic acid;
- $EF = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{bulk}}/N_{\text{bulk}})^3$

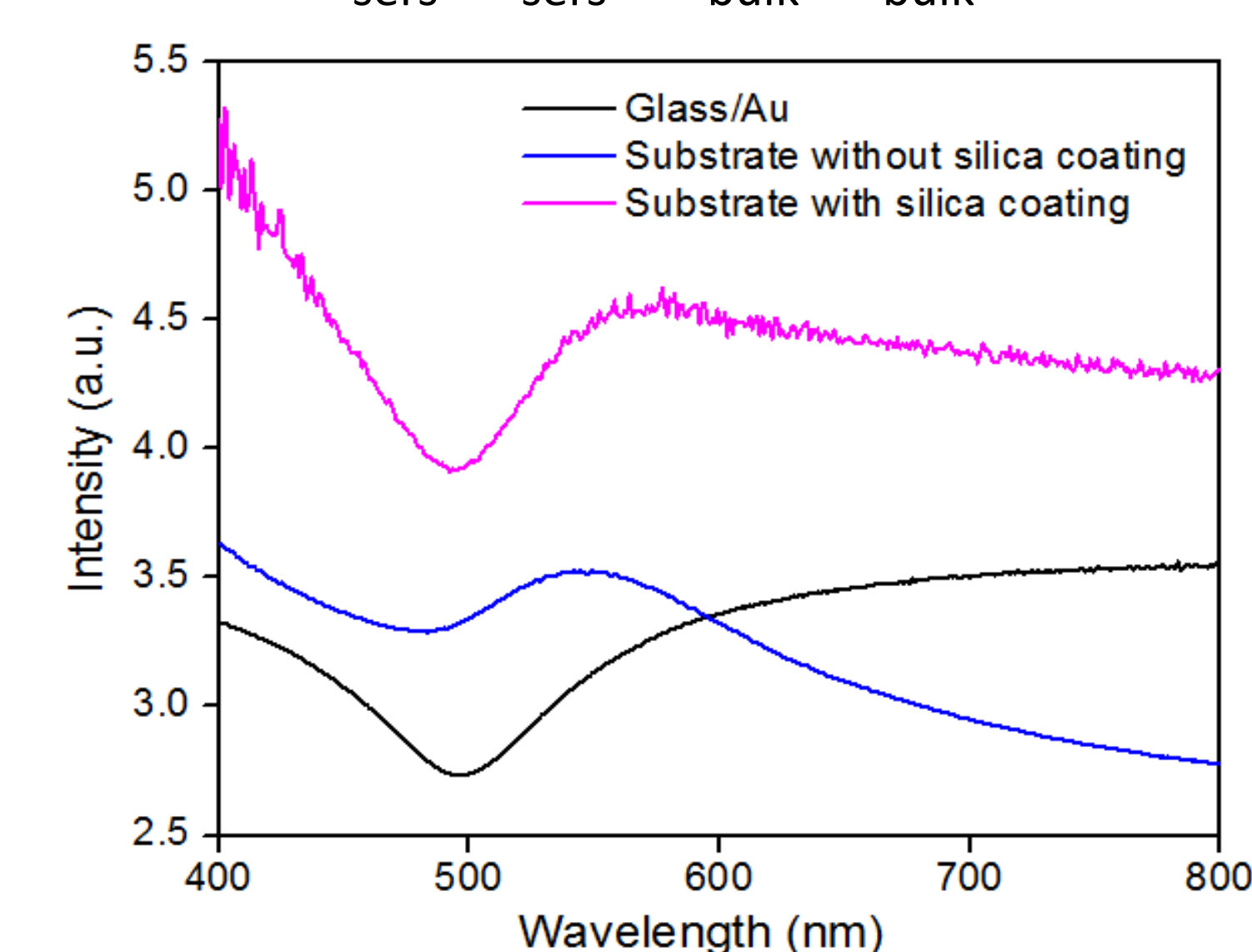


Figure 5. UV-Vis absorption of gold coated glass, substrate before and after silica coating.

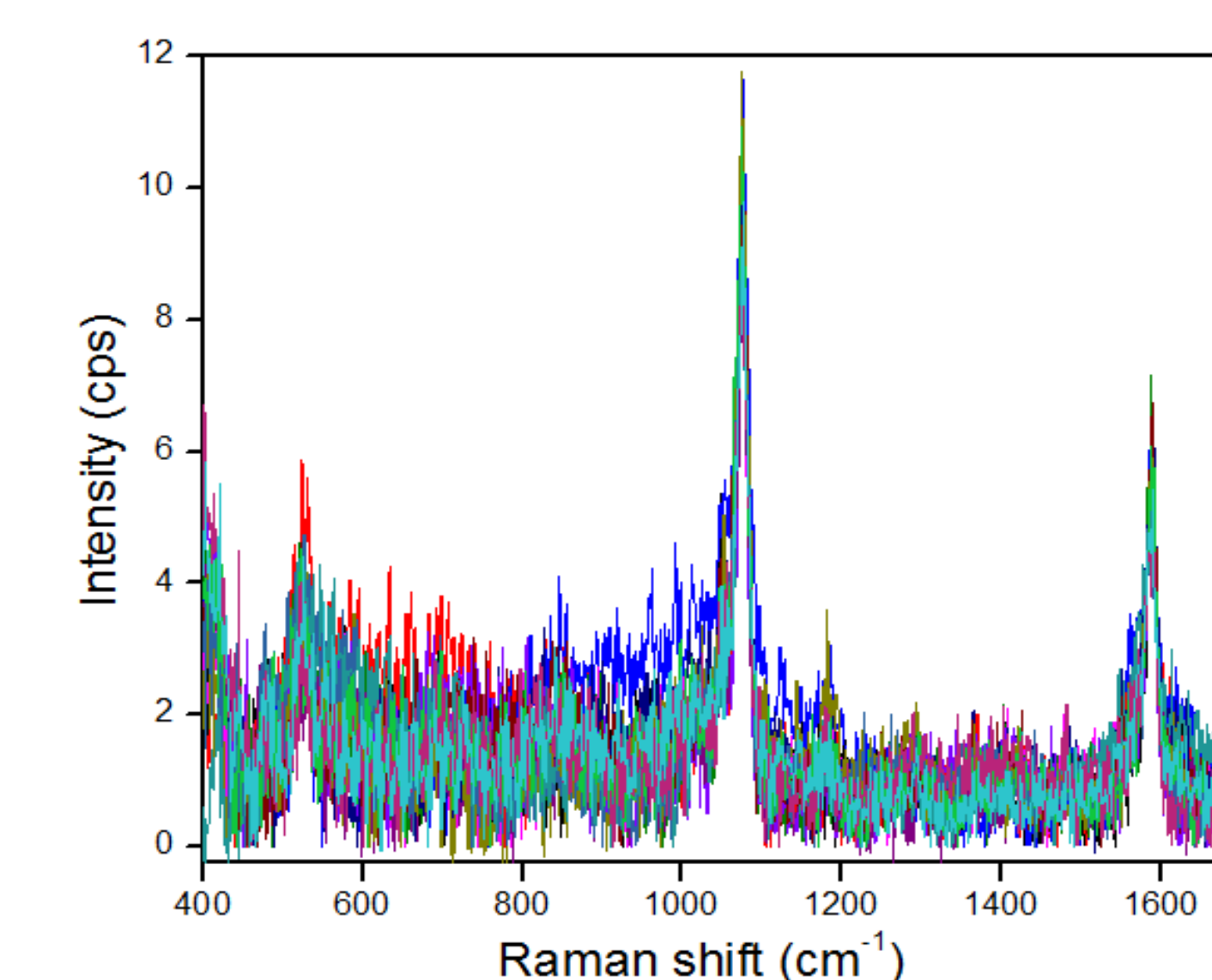


Figure 6. SERS spectra of 4-MBA (10^{-6} M) collected on 15 random spots on substrate.

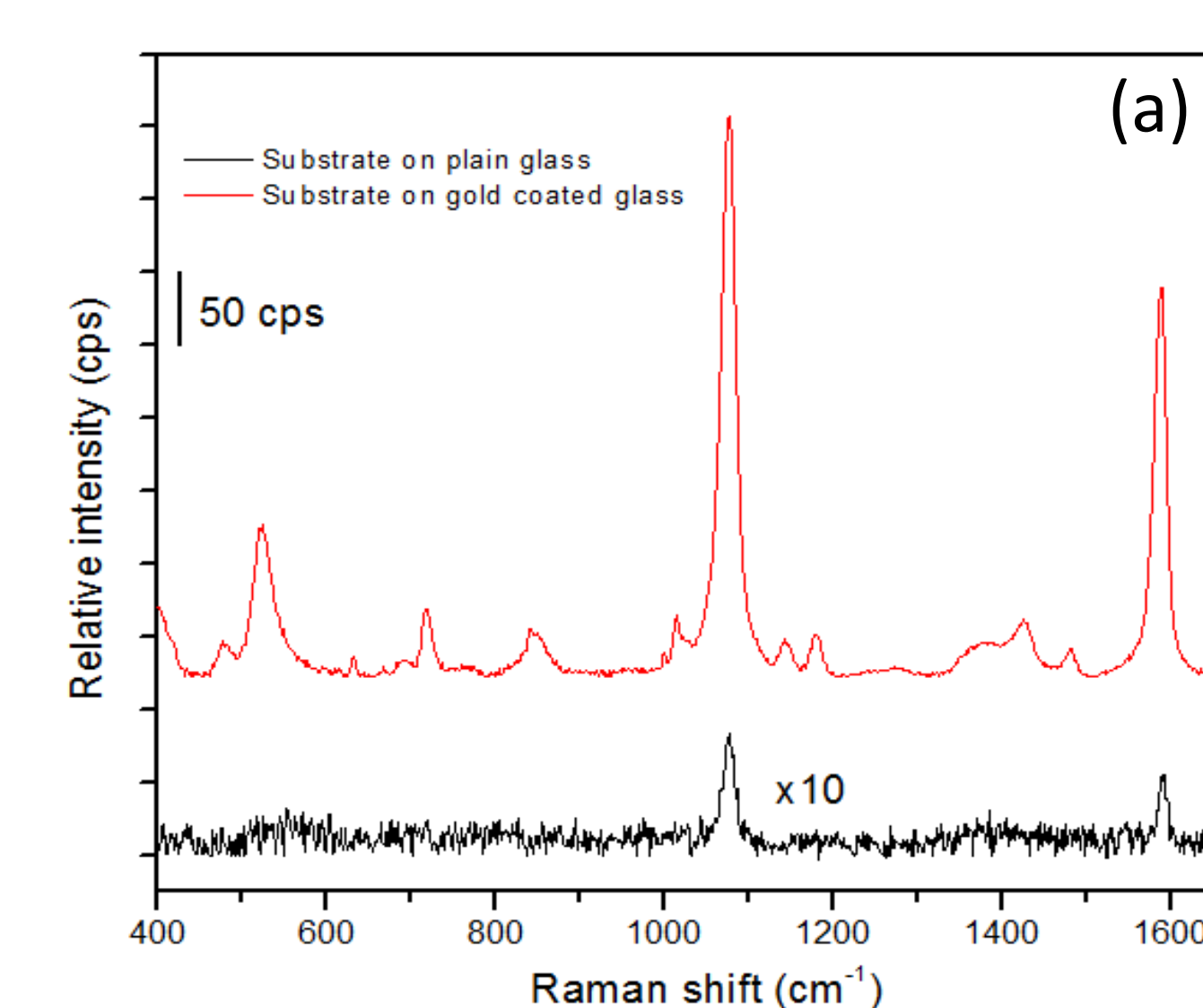


Figure 7. (a) SERS spectrum of 4-MBA 0.11M for substrate on gold coated glass and plain glass. (b) SERS spectrum of 10^{-3} M 4-MBA before and after silica coating.

Conclusion and Future works

- Hybrid materials of semiconductor/nobel metal that can provide reliable non-resonant SERS signal with low detection limit (14ppm) in NIR region.
- Wider range of application in industrial and commercial settings
- Optimize the morphology to get better improvement

References

1. Wittkamp, B. L.; Tilotta, D. C. *Anal. Chem.* **1995**, 67 (3), 600–605.
2. Karlowatz, M.; Kraft, M.; Mizalkoff, B. *Anal. Chem.* **2004**, 76 (9), 2643–2648.
3. E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *J. Phys. Chem. C*, 2007, 111, 13794–13803.

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