

Plasmon-free surface-enhanced Raman spectroscopy on TiO₂-graphene oxide inverse opal substrates

Luis E. Perez* and Dr. Elizabeth J. O. Atkinson

Chemistry Department, Linfield College, McMinnville, Oregon 97128-2829

Abstract

TiO₂-graphene oxide (GO) inverse opal materials were shown to be active plasmon-free surface enhanced Raman spectroscopy (SERS) substrates. The SERS activity of the substrates was analyzed using three different probe molecules: phenethylamine (PEA), methylene blue (MB), and 4-mercaptobenzoic acid (4-MBA). The morphology of the substrates was investigated by SEM and AFM. Prepared TiO₂-GO inverse opals substrates can be reused up to five times with minimal loss of signal, rendering them perfect candidates to be used as highly stable, low-cost, metal-free, recyclable SERS substrates.

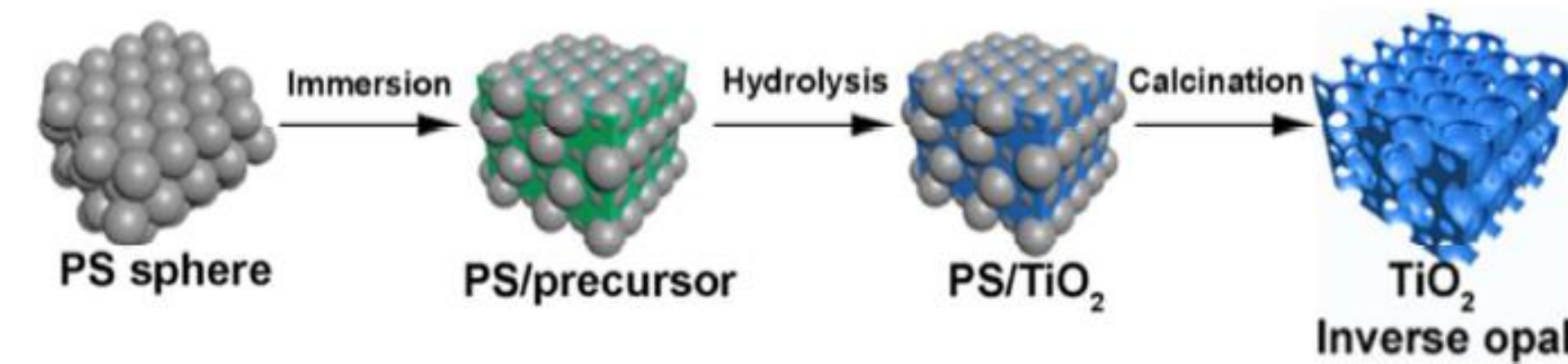


Figure 1. A template of polystyrene colloids is prepared and coated with the precursor solution. The solution is hydrolyzed to form a three-dimensional matrix, and polystyrene colloids are removed through calcination. The hollow structure left behind is the TiO₂ inverse opal crystal (1).

Background

Surface enhanced Raman spectroscopy (SERS) is a non-invasive technique that has been used since 1974 to characterize pigments, dyes, and other substances. Currently available SERS substrates rely on the use of noble metals to enhance the Raman signal through surface plasmon resonance, but they are expensive, have a short shelf life, and can only be used once. Macroporous TiO₂ materials, graphene, graphene oxide (GO), and GO- TiO₂ composite materials have been shown to be active plasmon-free SERS substrates (2-4). Qi et al. reported the most successful example of these attempts: plasmon-free SERS activity from a TiO₂ photonic microarray caused by enhancing light-matter coupling. However, inverse opal materials have not been used for plasmon-free SERS ever since that first report, and the viability of GO- TiO₂ composite macroporous structures (i.e. inverse opal crystals) as SERS substrates has not been investigated.

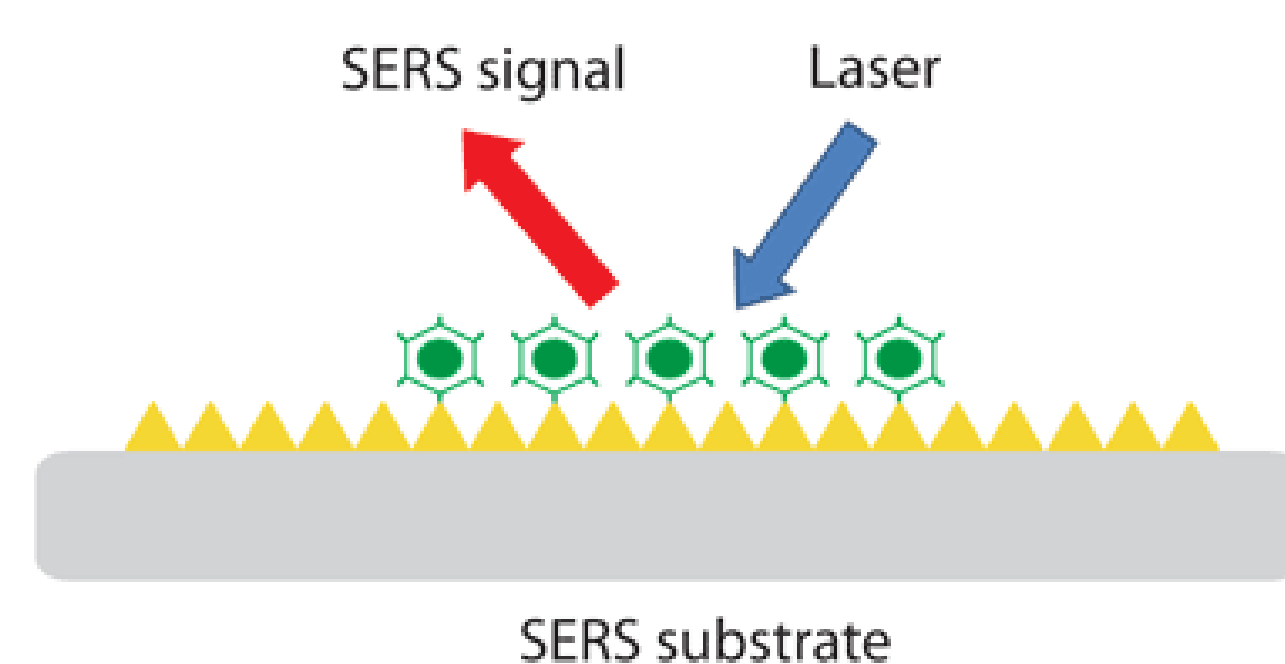


Figure 2. Illustration of surface-enhanced Raman scattering effect.

Raman Results

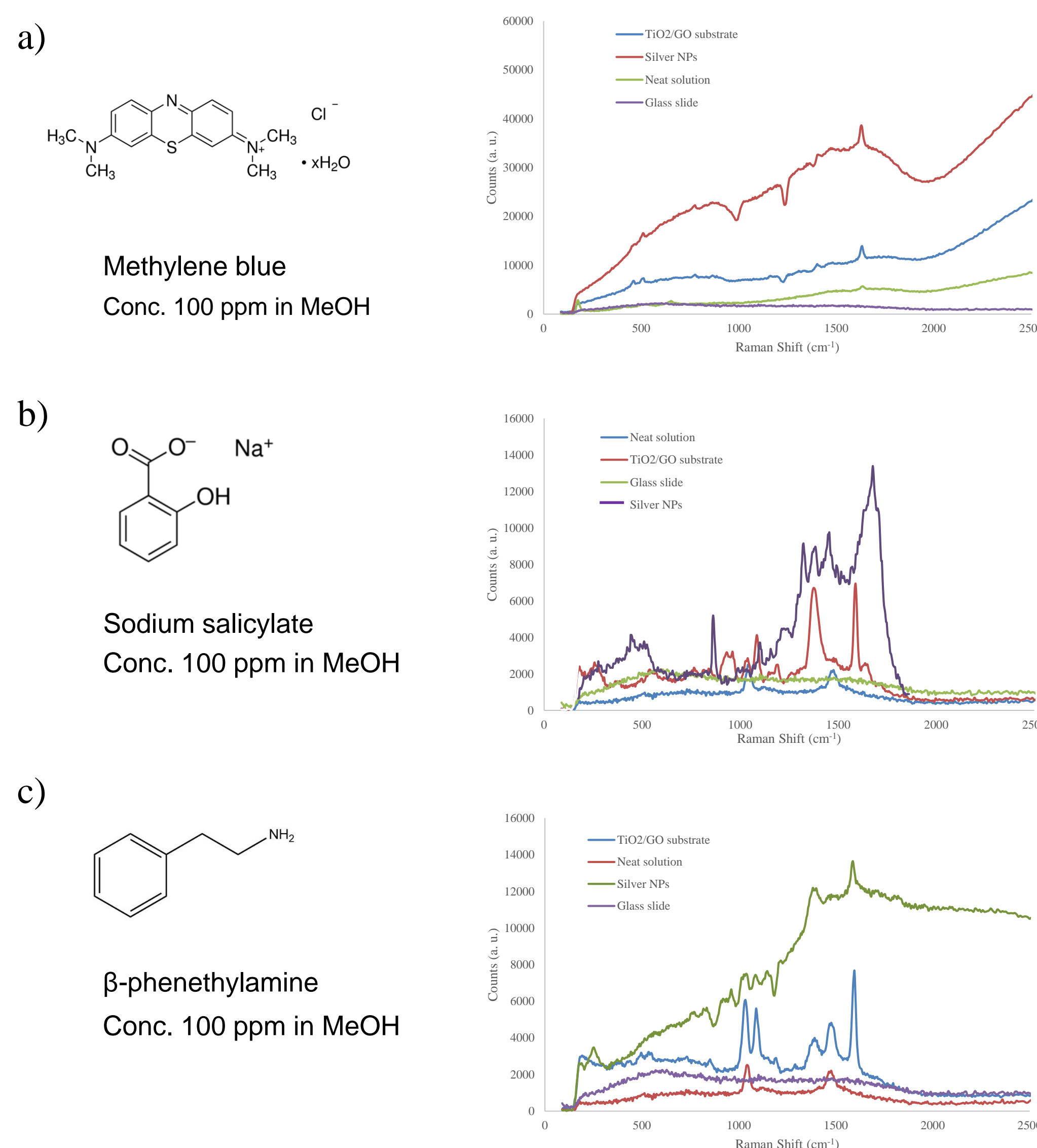


Figure 3. Raman spectra of a) methylene blue, b) sodium salicylate, and c) β -phenethylamine (PEA) on a glass slide, a glass slide with silver colloids, as a neat solution, and on prepared inverse opal substrates.

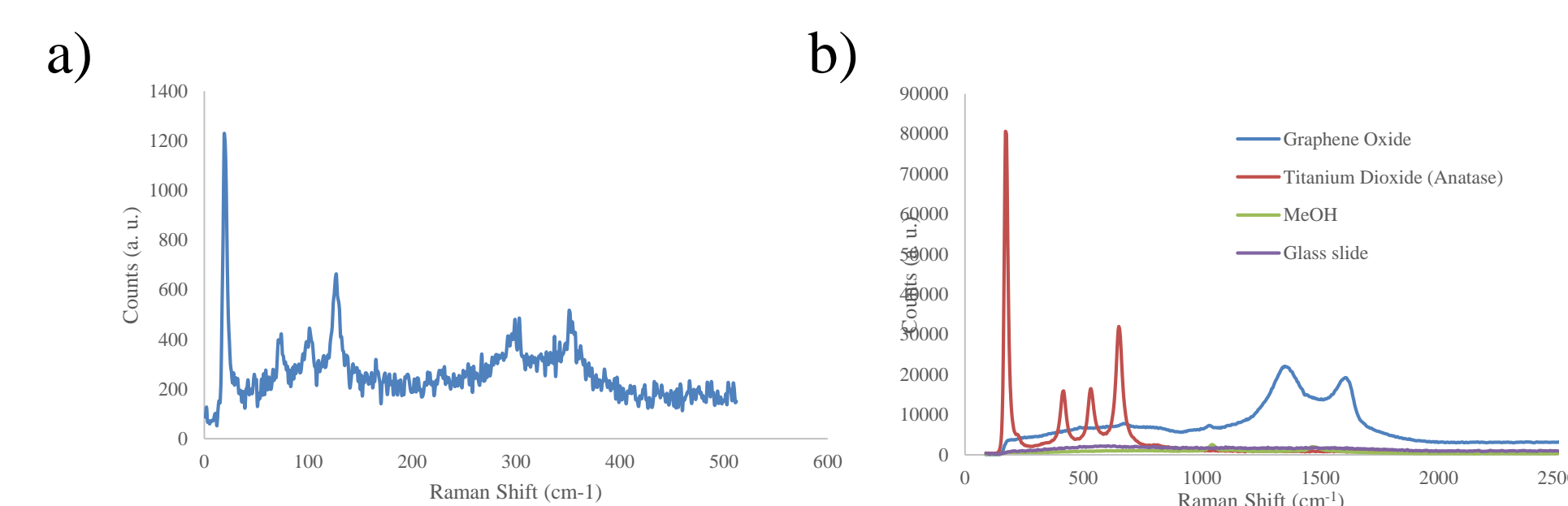


Figure 4. Raman spectra of prepared a) inverse opal substrate, b) relevant substances.

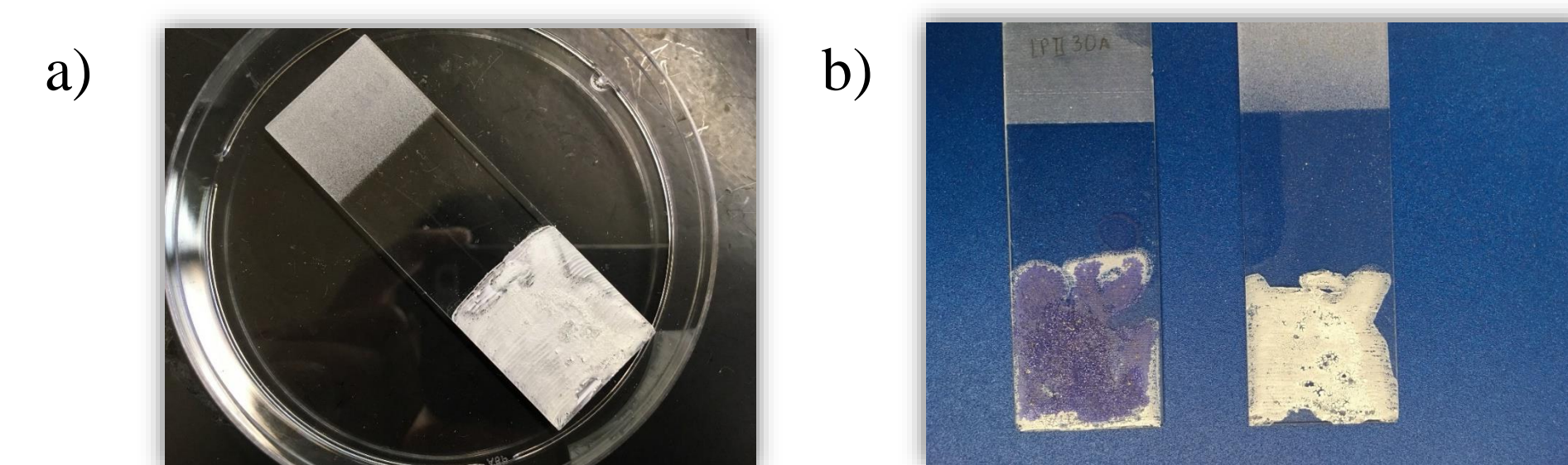


Figure 5. Representative pictures of a) a TiO₂-GO prepared opal substrate and b) an inverse opal substrate after addition of methylene blue (right) and sodium salicylate solution (left).

AFM and SEM Results

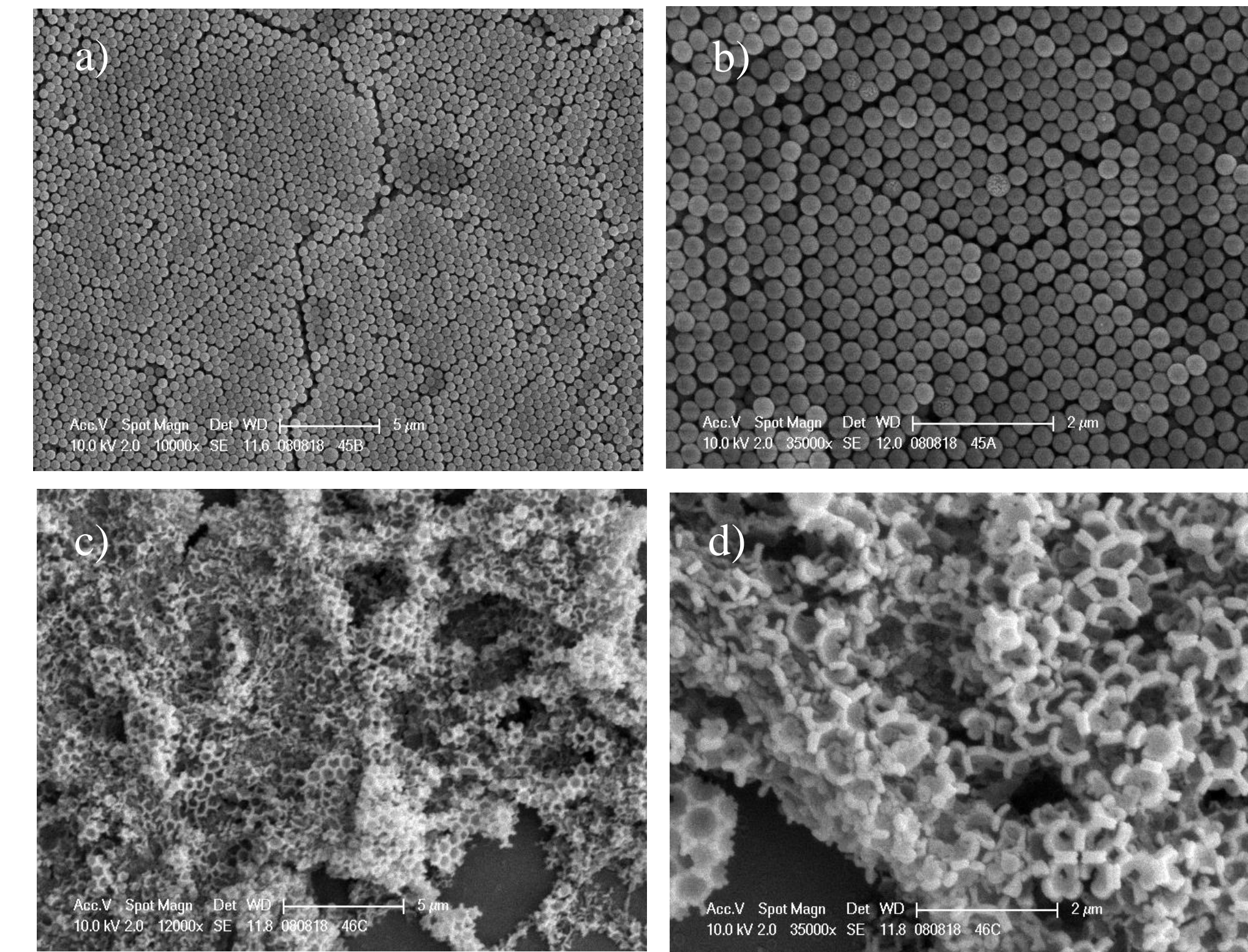


Figure 6. Surface images obtained using scanning electron microscopy (SEM) of a-b) polystyrene colloidal crystal with mean particle size 0.30 μ m, c-d) titanium dioxide-graphene oxide inverse opal.

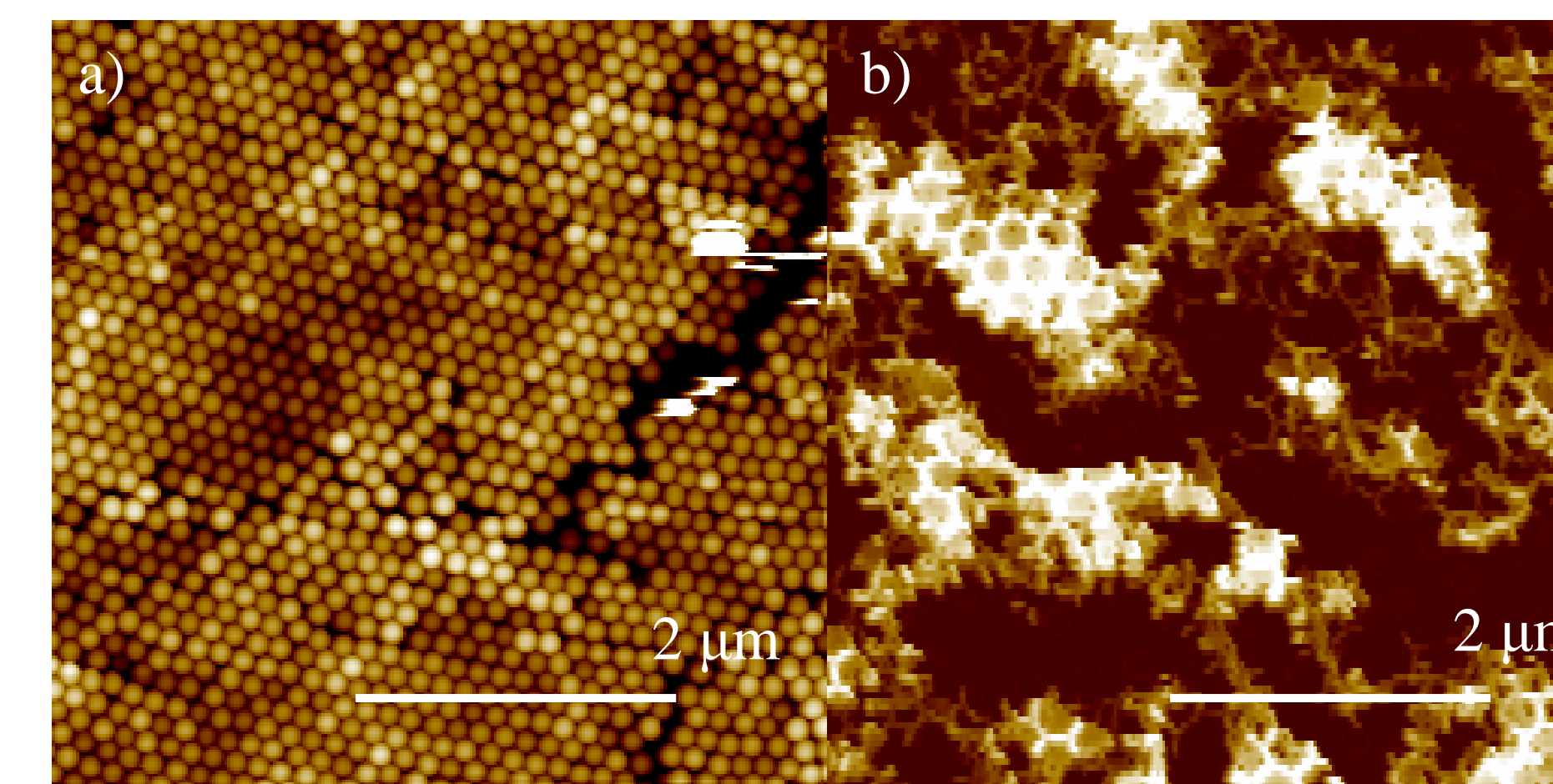


Figure 7. Atomic force microscopy (AFM) images showing the topography of a) polystyrene colloidal crystal with mean particle size 0.30 μ m and b) titanium dioxide-graphene oxide inverse opal.

Conclusion

In comparison to silver colloids, prepared inverse opal substrates exhibit Characterization by SEM (Figure 4) and AFM (Figure 5) show the characteristic structure of inverse opal materials. The enhancement of the signal may be attributed to enhanced light-matter interactions resulting from the repeatedly scattered laser light among the periodic voids (1). Prepared TiO₂-GO inverse opal substrates were shown to exhibit plasmon-free surface-enhanced Raman scattering, as well as being shown to be reusable up to five times with minimal loss of signal.

Experimental

Chemicals and materials. Titanium (IV) isopropoxide (TTIP, 98%), methanol (≥ 99.9), ammonium hydroxide (30%), acetylacetone (98%), absolute ethanol, latex beads/polystyrene dispersion in water (0.3, 0.46, 0.6 μ m) and graphene oxide (2 mg/mL, dispersion in water) (GO) were purchased from Sigma Aldrich (Milwaukee, WI).

Raman/UV-Vis measurements. Raman spectra were obtained with a custom-built Raman spectrometer using a 150mW, 532nm Spectra-Physics Excelsior laser, a CVI Digikrom 0.25 m monochromator (600 g/mm grating, 50 μ m slit width), and an Apogee thermoelectrically cooled CCD. Data were acquired using KestrelSpec at 5 second acquisition times and spectra were analyzed using Origin 9.4 64-bit for Windows.

Titanium (IV) isopropoxide-graphene oxide (TTIP-GO) precursor solution Titanium (IV) isopropoxide (50 mL), absolute ethanol (40 mL), acetylacetone (0.89 mL) and graphene oxide (2% w/v, 0.50 mL) were stirred for one minute. HCl (0.30 M, 4.87 mL) was added to mixture, stirred for two hours, and stored in the dark.

Preparation of substrates

1. Glass slides were cleaned with a piranha solution (3:1 conc. H₂SO₄ to 30% H₂O₂)
2. Cleaned slides were coated by vertical deposition in a 0.08% w/v dispersion of polystyrene (PS) beads in water at 75 °C overnight to produce a PS colloidal template.
3. PS colloidal templates were submerged in a TTIP-GO precursor solution and heated at 75 °C overnight.
4. Coated PS colloidal templates were calcinated at 450 °C for two hours in a Thermolyne Type 1500 Furnace (1 °C/min heating rate & cooling rate)

Testing substrates and gauging their reusability

1. Sample solution was added to the substrate dropwise and allowed to dry.
2. Raman spectra of substrates with sample were taken
3. Reusability of substrate was assessed (Figure 8)
4. Substrates dried under a nitrogen flow and analyte added again

Preparation of β -phenethylamine

Nitromethane (7.15 mL), benzaldehyde (10.2 mL), butylamine (0.5 mL), and absolute ethanol were refluxed for an hour. Precipitate was recrystallized from absolute ethanol to yield yellow needle-like crystals of phenyl-2-nitroethene (6.322 g, 63%, mp 57.5-59 °C). Phenyl-2-nitroethene (2.0 g) was dissolved in dry THF (15 mL) and added dropwise to a mixture of lithium aluminum hydride (2.8 g) and dry THF (35 mL) and refluxed for one hour. Reaction mixture was cooled to RT and quenched with isopropyl alcohol (3.0 mL), NaOH (1 M, 3mL) and water (6 mL). The reaction was filtered to remove particulate matter, washed with THF (100 mL), and concentrated under vacuum.

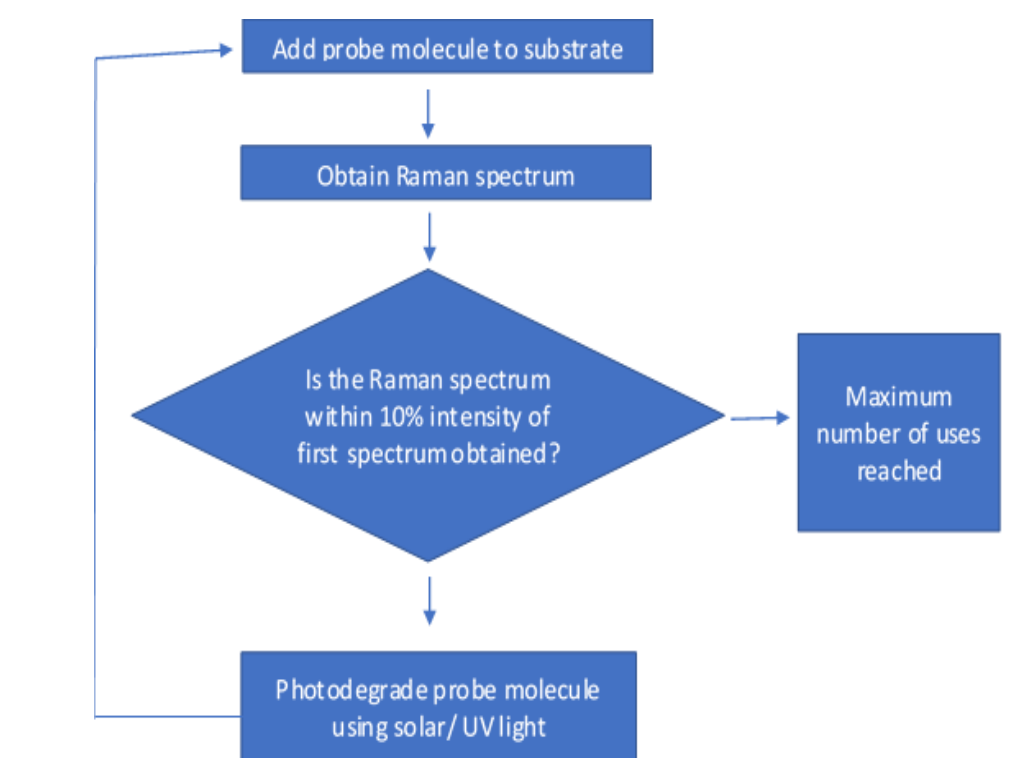


Figure 8. General flowchart used to determine the maximum number of uses that could be achieved for prepared inverse opal substrates.

References

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Acknowledgments

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