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Development of nanoparticle catalysts and total internal reflection (TIR) Raman spectroscopy for improved understanding of heterogeneous catalysis

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Appendix: Chapter 5

Total internal reflection (TIR) Raman spectra recorded for platinum/polyvinylpyrrolidone nanoparticle (platinum/PVP np) samples both before and after plasma cleaning

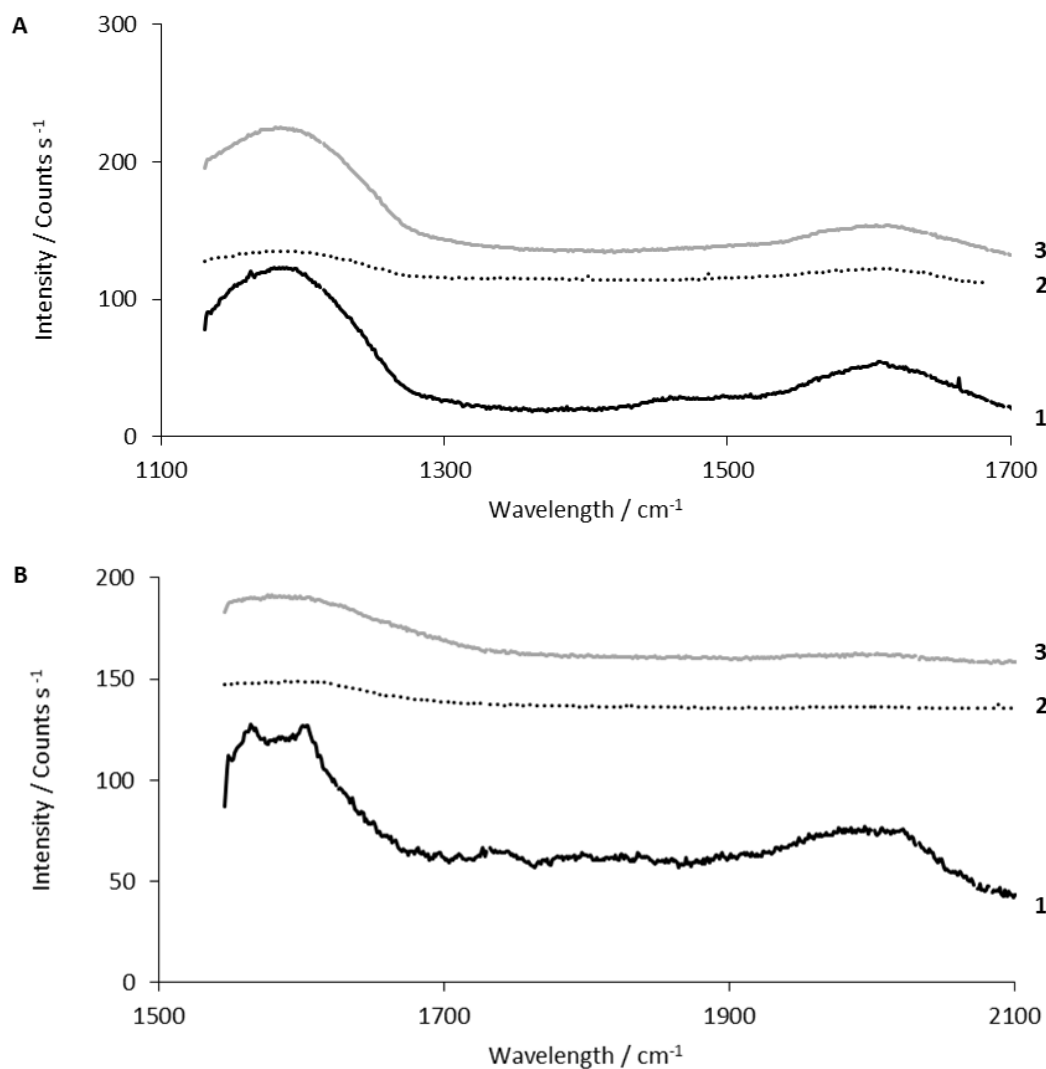


Figure 5A.1. TIR Raman spectra for the following samples with no gas flow 1- a clean silica hemisphere, 2- platinum/PVP nps (Section 2.2.1.1) LB deposited on a silica hemisphere (Section 2.2.5.9), 3- platinum/PVP nps LB deposited on a silica hemisphere and plasma cleaned for 2 min). Figures 5A.1 A-B and 5A.2 A show regions at which spectral features were expected. Spectra were taken for a laser power of 600 mW with an exposure time of 7.5 s for 10 frames. Spectra have been offset vertically for clarity. Single point data, attributed to stray electronic signals, have been removed as part of data processing. All spectra collected with 532 nm excitation wavelength.

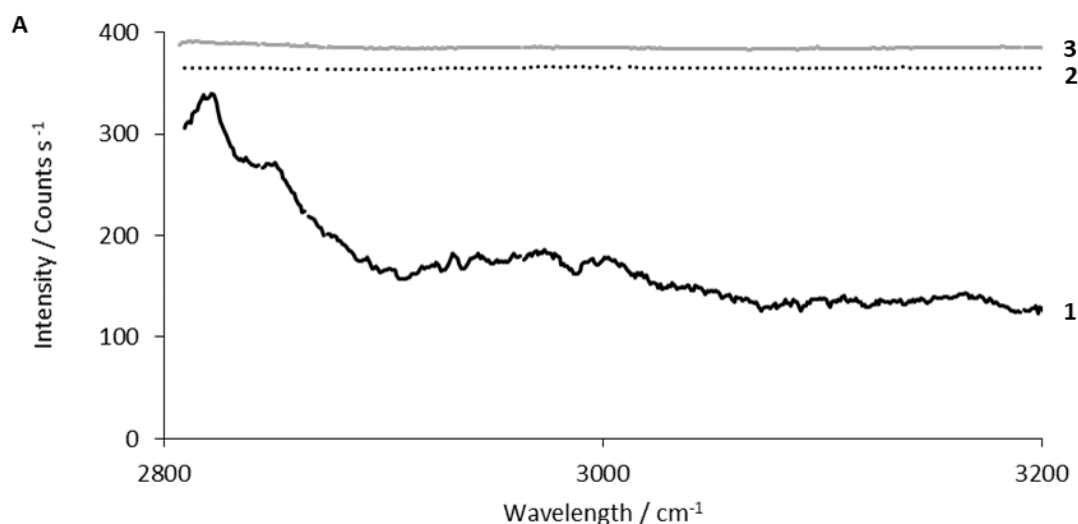


Figure 5A.2. TIR Raman spectra for the following samples with no gas flow 1- a clean silica hemisphere, 2- platinum/PVP nps (Section 2.2.1.1) LB deposited on a silica hemisphere (Section 2.2.5.9), 3- platinum/PVP nps LB deposited on a silica hemisphere and plasma cleaned for 2 min. Figures 5A.1 A-B and 5A.2 A show regions at which spectral features were expected. Spectra were taken for a laser power of 600 mW with an exposure time of 7.5 s for 10 frames. Spectra have been offset vertically for clarity. Single point data, attributed to stray electronic signals, have been removed as part of data processing. All spectra collected with 532 nm excitation wavelength.

TIR Raman spectra for platinum/oleylamine nanoparticles (platinum/OAm nps) taken at the beginning (the first 50 frames of data) and towards the end of the exposure (the last 50 frames)

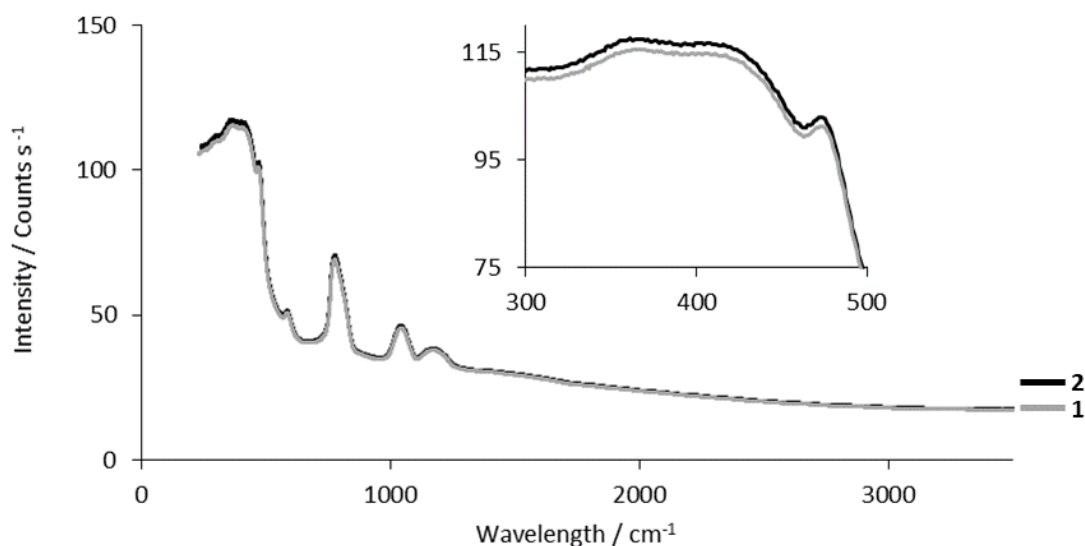


Figure 5A.3. TIR Raman spectra taken for platinum/OAm nps (Section 2.2.1.2) for comparison of the 1- first 50, and 2- last 50 frames. Both spectra were taken for a laser power of 600 mW with an exposure time of 20 s for 100 frames. All spectra were taken using grating 3 with a slit width of 100 μm . Spectra have been offset vertically for clarity.

Division spectra for TIR Raman spectroscopy of monolayer deposited nanoparticle samples

The curvature seen in the spectra (Figure 5A.4) at low wavelength (approximately 1200-1300 cm^{-1}) is not a spectral feature (as indicated by the background fitted) and is due to remaining silica background not removed by division of the clean silica hemisphere. The clean silica hemisphere typically displays much higher intensity bands due to the lack of material covering the surface being probed and therefore masking signal, as well as due to differences in the positioning of the laser spot. For a hemisphere coated with a monolayer of a nanoparticle the laser spot will typically be placed at the surface for the coated material rather than directly at the silica interface.

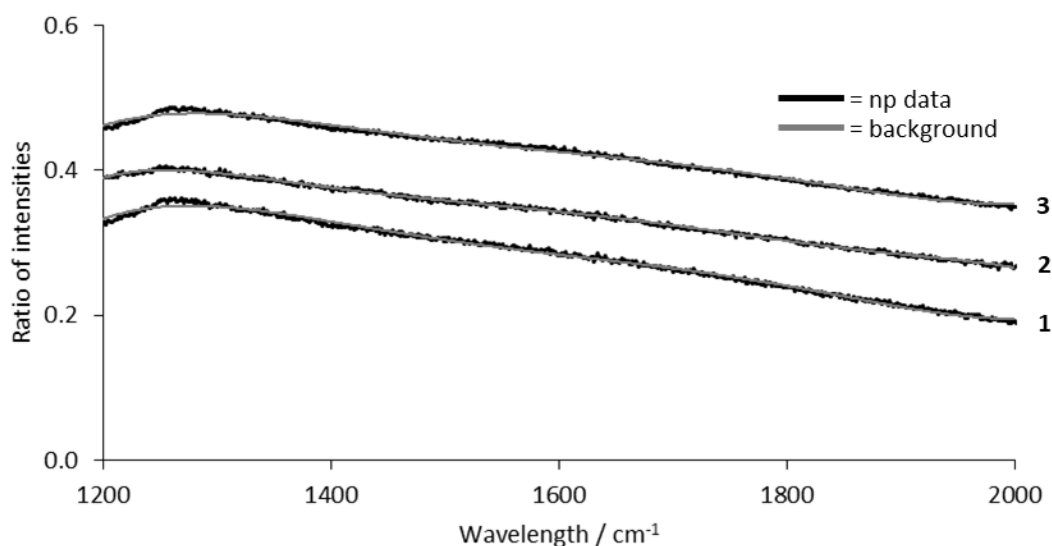


Figure 5A.4. Difference spectra for TIR Raman spectra taken in the region of 1200-2000 cm^{-1} for the following nanoparticle samples deposited at a monolayer concentration upon a silica hemisphere using LB techniques (Section 2.2.5.9) 1- cobalt/oleic acid nanoparticles (cobalt/OAc nps, see Section 2.2.1.3), 2- copper/oleylamine nanoparticles (copper/OAm nps, Section 2.2.1.5), 3- platinum/oleylamine nanoparticles (platinum/OAm nps, Section 2.2.1.2). All spectra have been divided by spectra of the clean silica hemisphere in order to allow for extraction of low intensity features. The following equations were used for each background 1- $y = 8E-15x^5 - 7E-11x^4 + 2E-07x^3 - 0.0004x^2 + 0.2851x - 90.217$, 2- $y = -2E-17x^6 + 2E-13x^5 - 7E-10x^4 + 2E-06x^3 - 0.0019x^2 + 1.2074x - 320.57$, 3- $y = 7E-15x^5 - 6E-11x^4 + 2E-07x^3 - 0.0003x^2 + 0.2365x - 74.604$. Spectra 1 was taken for a laser power of 600 mW with an exposure time of 20 s for 50 frames. Spectrum 2, and 3 were taken at a laser power of 600 mW with an exposure time of 20 s for 100 frames. All spectra were taken using grating 3 with a slit width of 100 μm . Spectra have been offset vertically for clarity.

Sensing nanoparticles *in situ*, blank hemispheres with gas feeds unprocessed data

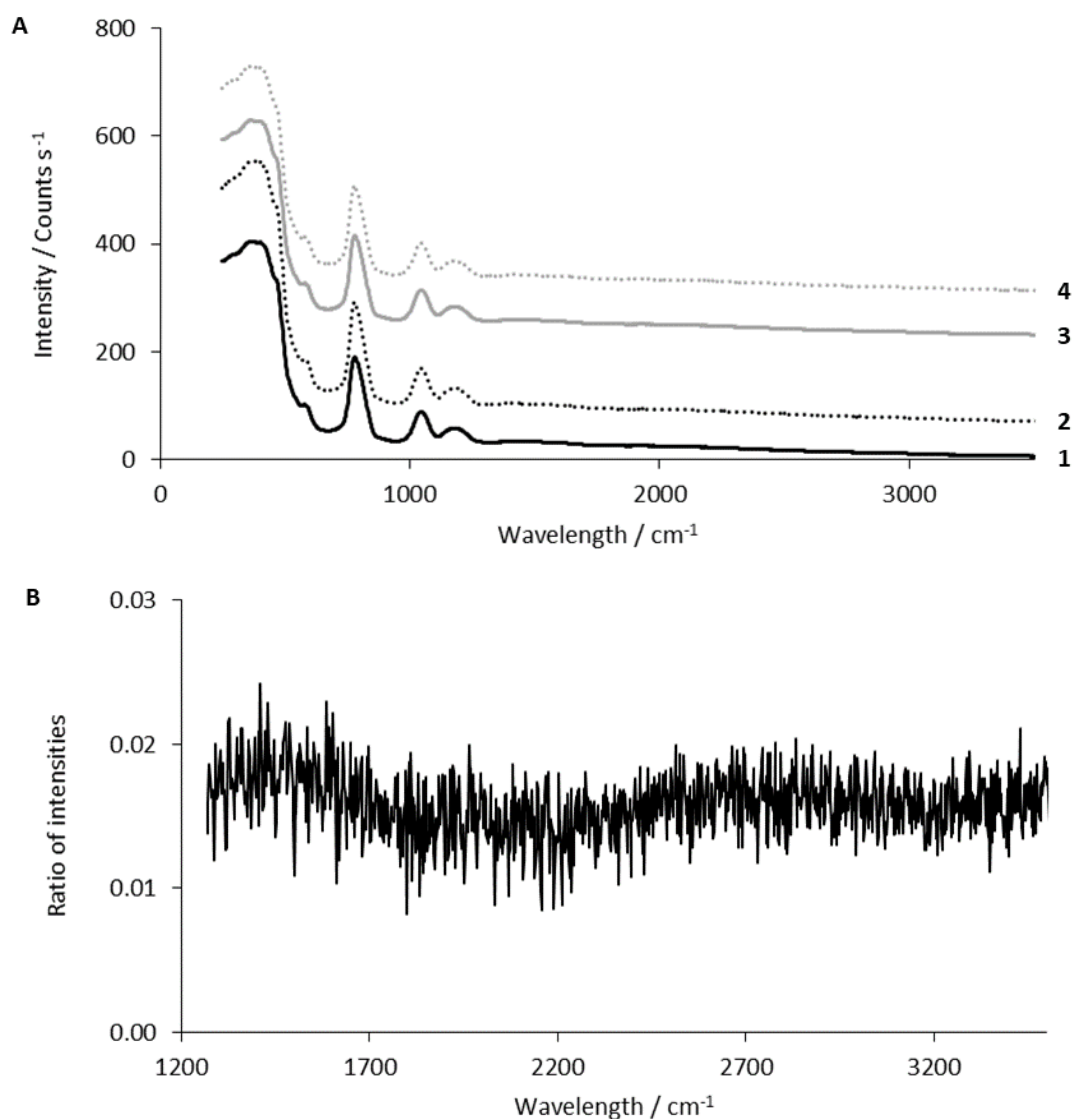


Figure 5A.5. A) TIR Raman spectra taken for a silica hemisphere in the presence of the following gas feeds 1- no gas feed, 2- 0.83 bar of helium, 3- 0.83 bar of helium, and 0.13 bar of hydrogen, 4- 0.83 bar of helium, 0.13 bar of hydrogen and 0.04 bar of ethylene. Both spectra were taken using grating 2 with a slit width of 200 μm in order to maximise peak intensity. Spectra were taken at a laser power of 600 mW with an exposure time of 20 s for 50 frames. Spectra have been offset vertically for clarity.

B) Difference spectra obtained from the TIR Raman spectra taken for a clean silica hemisphere in the presence of 0.83 bar of helium. The spectra has been divided by spectra of the clean silica hemisphere in the absence of any gas flow in order to allow for extraction of low intensity features. Spectra was taken using grating 2 with a slit width of 200 μm in order to maximise peak intensity. Both spectra were taken at a laser power of 600 mW with an exposure time of 20 s for 50 frames. The spectra has been offset vertically for clarity.