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

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Appendix: Chapter 3

Calculation of the amount of oleylamine capping agent required to give full coverage of the silver surface

For a silver nanoparticle with a diameter of 6 nm (Chapter 3, Section 3.1.2.1), the total surface area available for the capping agent to bind to is 1.13×10^{-16} m^2 per particle. For capping agent binding in the head-on orientation (Figure 3A.1) an estimation of the maximum number of capping agents bound can be made. The number of capping agents bound to one 6 nm diameter silver nanoparticle, can be determined from the van der Waals dimensions of the head group. Since such data was not readily available for oleylamine and oleic acid calculations made use of values for the thiol group instead. This was on the basis that the thiol was likely an upper limit (would be larger than the amine). For a typical thiol head group the van der Waals dimensions were 5.29×10^{-20} m^2.[1]

This gives an approximation of 2140 capping agents which could bind head on around one 6 nm silver nanoparticle.

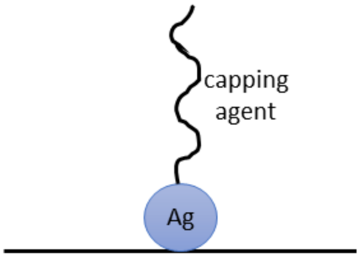

Figure 3A.1. Schematic of silver nanoparticle with oleylamine or oleic acid capping agents bound in a head on fashion.

The number of silver atoms in the particle of diameter 6 nm can be estimated. The fcc unit cell for silver is shown below in Figure 3A.2.

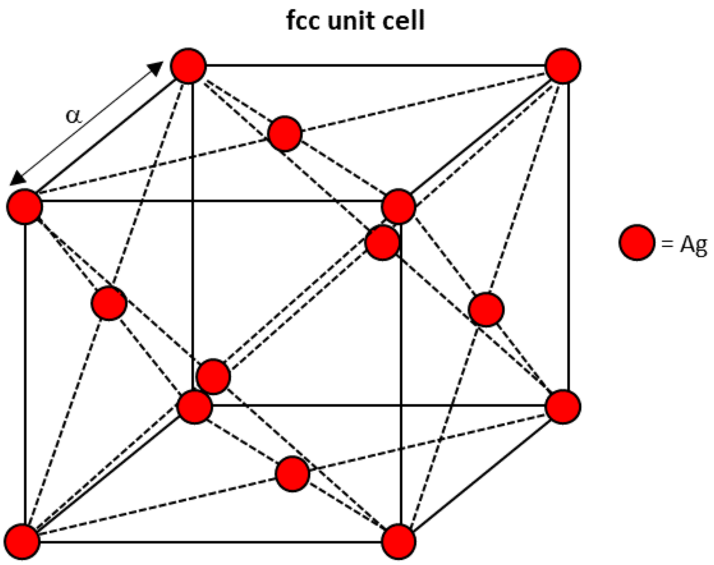

Figure 3A.2. Diagram of fcc unit cell for silver.

The lattice vector α can be calculated from the atomic radius (R) for silver using Equation 3A.1.

$$\boldsymbol{a = 2\sqrt{2}R} \qquad \textit{Equation 3A.1}$$

Inputting of the value of R for silver allows to calculate α.

$$a = 2\sqrt{2}(1.72 \times 10^{-10}\, m)$$

The volume occupied by an FCC unit cell (V) can be given by Equation 3A.2.

$$\boldsymbol{V = a^3} \qquad \text{Equation 3A.2}$$

$$V = ((2\sqrt{2})(1.72 \times 10^{-10}\, m))^3$$

$$V = 1.15 \times 10^{-28}\, m^3$$

The volume (V_S) occupied by the silver nanoparticle of diameter 6 nm can then be calculated, as shown in Equation 3A.3.

$$\boldsymbol{V_s = \frac{4}{3}\pi r^3} \qquad \textit{Equation 3A.3}$$

$$V_s = \frac{4}{3}\pi(3 \times 10^{-9}\, m)^3$$

$$V_s = 1.13 \times 10^{-25}\, m^3$$

Therefore the number of silver fcc unit cells (N) which can fit in the 6 nm nanoparticle is given by Equation 3A.4.

$$\boldsymbol{N} = \frac{\boldsymbol{V_s}}{\boldsymbol{V}} \qquad \textit{Equation 3A.4}$$

$$\mathrm{N} = \frac{1.13\ \times 10^{-25}\, m^3}{1.15\ \times 10^{-28}\, m^3}$$

N= 983 Given that 4 silver atoms occupy one unit cell this gives a value of approximately 3930 copper atoms per 6 nm nanoparticle.

The molar ratio of capping agent:silver required to only fully saturate the surface of the copper nanoparticle based on the assumptions above for a 6 nm particle is therefore around 1 : 2. Therefore the 1:1 silver to capping agent ratio used in Fourier Transform infrared (FTIR) spectroscopic studies in Section 3.1.2.2 represented the upper limit of capping agent bound to metal.

Langmuir Blodgett (LB) trough deposition, of nanoparticles onto silicon wafers or silica hemispheres for bulk and total internal reflection (TIR) Raman spectroscopy

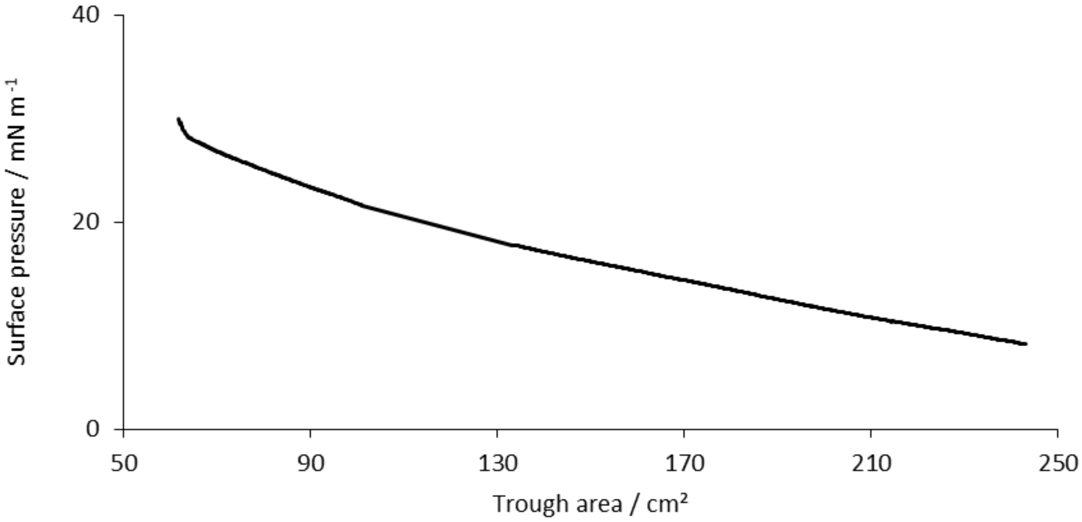

Figure 3A.3. LB trough isotherm experiment recorded for silver nanoparticles, showing surface pressure against the trough area. The isotherm was recorded with a low starting surface pressure.

X-ray photoelectron spectroscopy (XPS) investigation of platinum/polyvinylpyrrolidone nanoparticles (platinum/PVP nps) LB deposited onto substrates

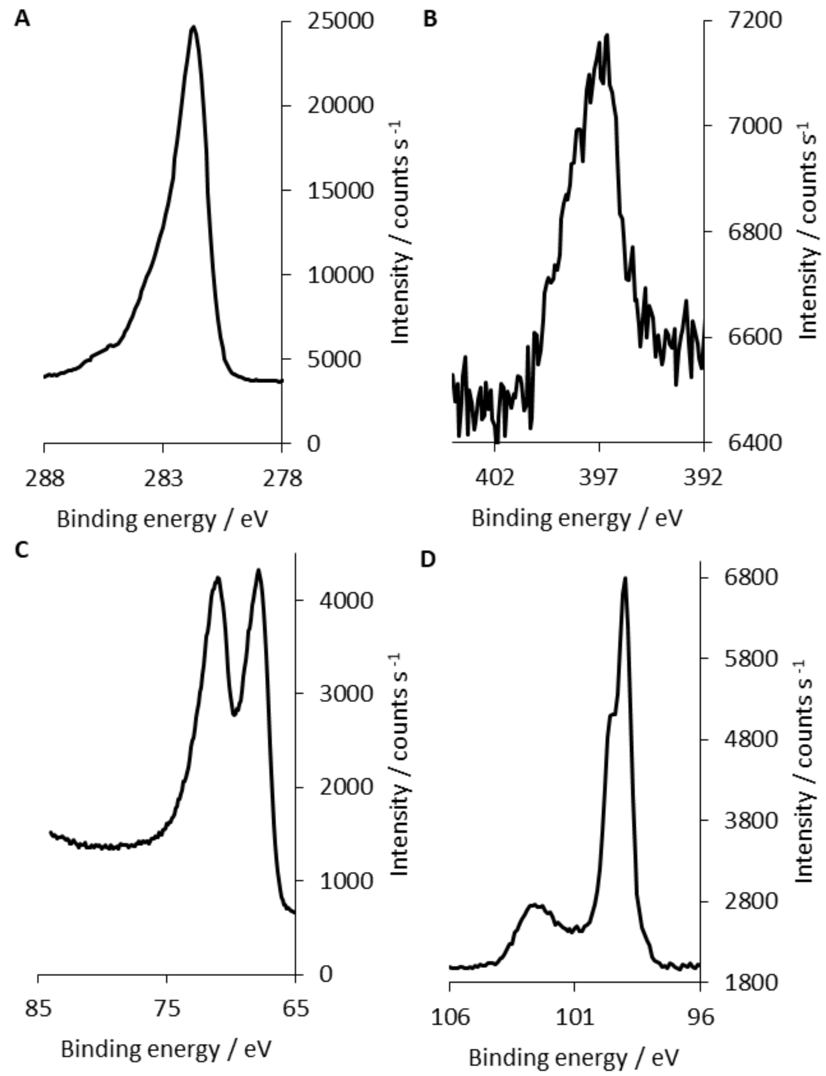

Figure 3A.4. XP spectra for sample two of three for platinum/PVP nps supported using LB techniques upon a silicon wafer (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

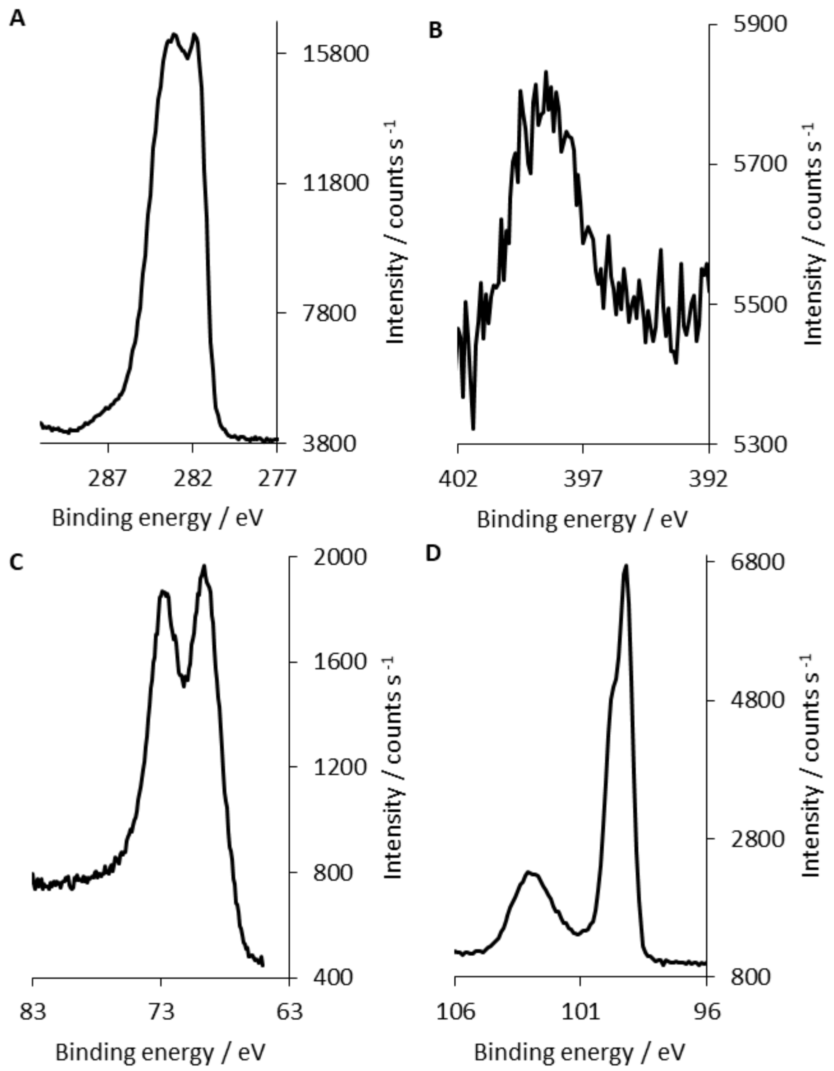

Figure 3A.5. XP spectra for sample three of three for platinum/PVP nps supported using LB techniques upon a silicon wafer (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

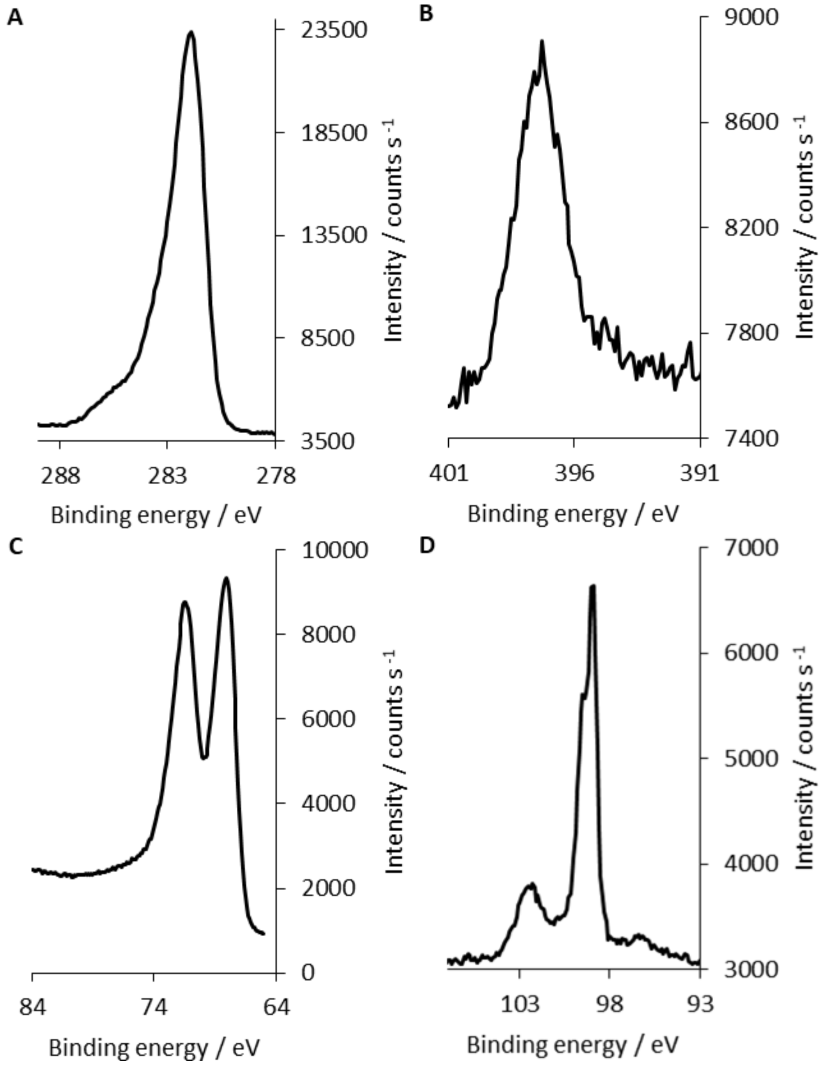

Figure 3A.6. XP spectra for sample one of three for platinum/PVP nps supported using LB techniques upon a silicon wafer (with two dippings of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

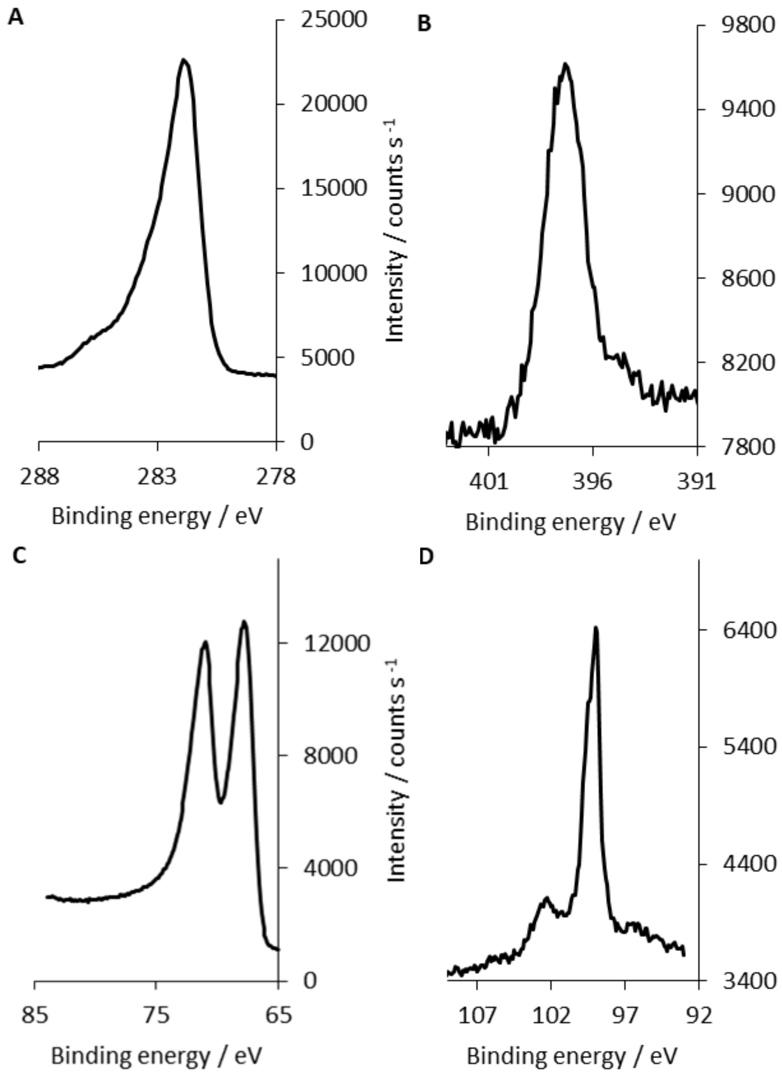

Figure 3A.7. XP spectra for sample two of three for platinum/PVP nps supported using LB techniques upon a silicon wafer (with two dippings of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

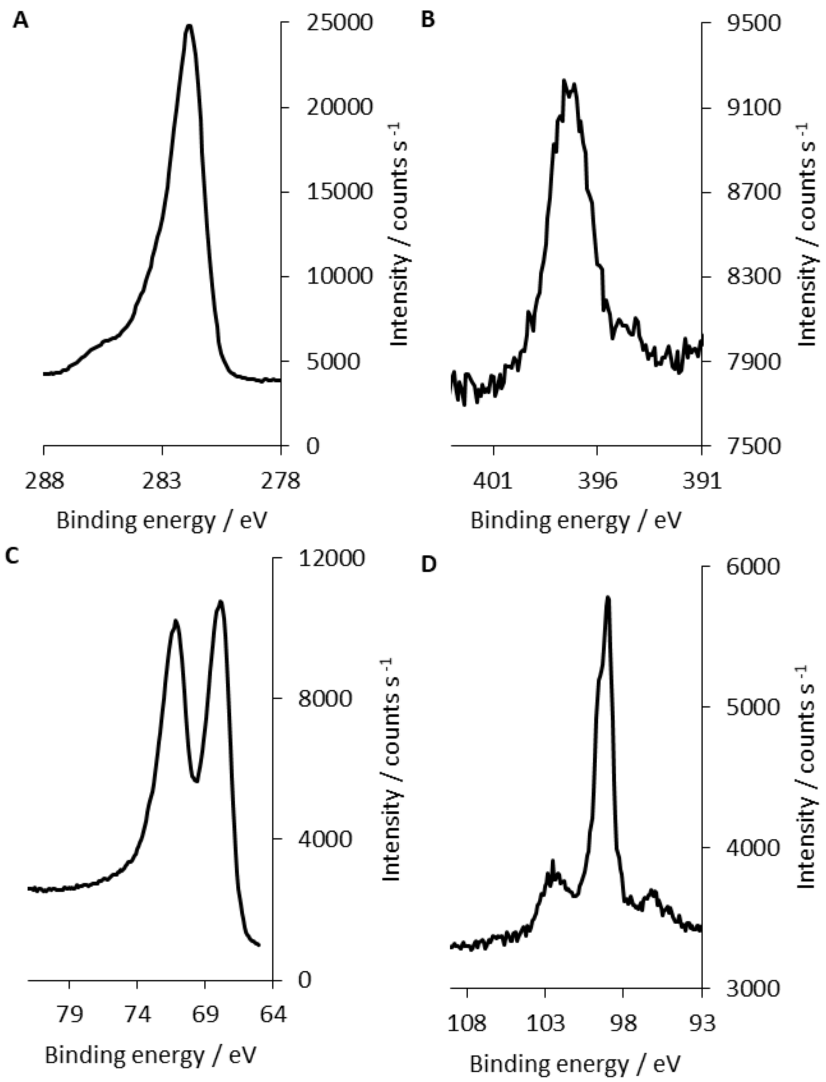

Figure 3A.8. XP spectra for sample three of three for platinum/PVP nps supported using LB techniques upon a silicon wafer (with two dippings of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

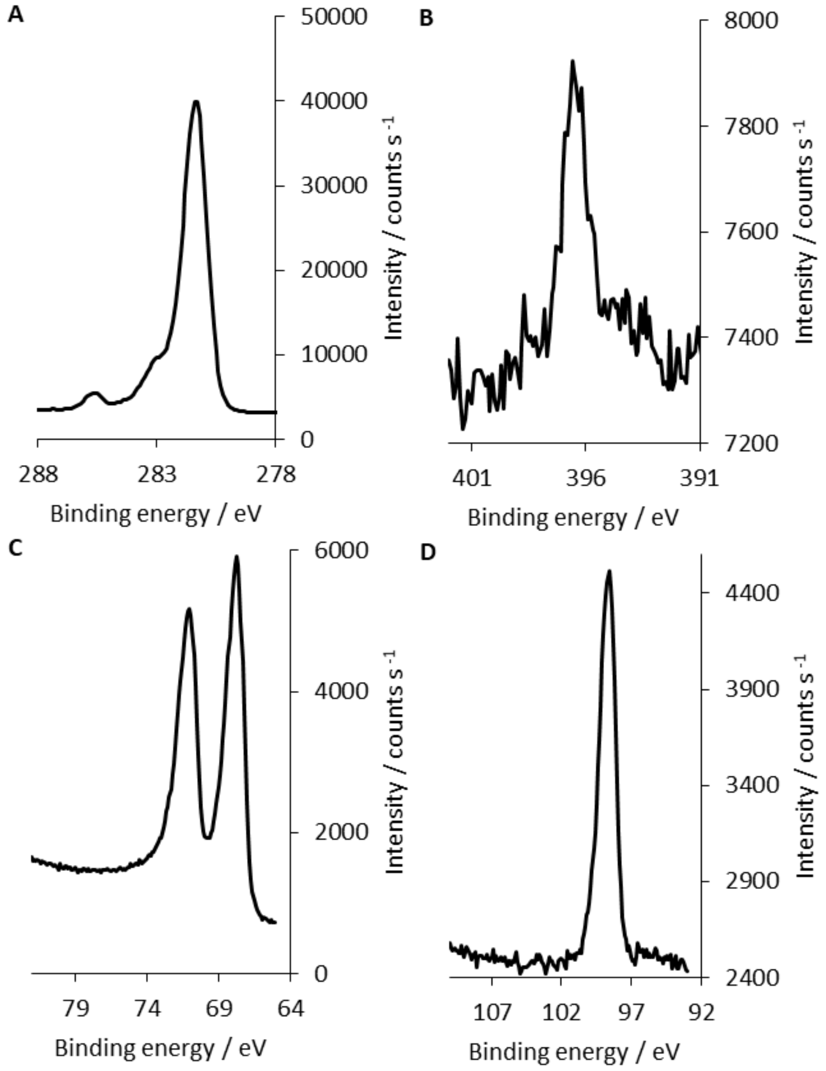

Figure 3A.9. XP spectra for sample one of five for the first five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

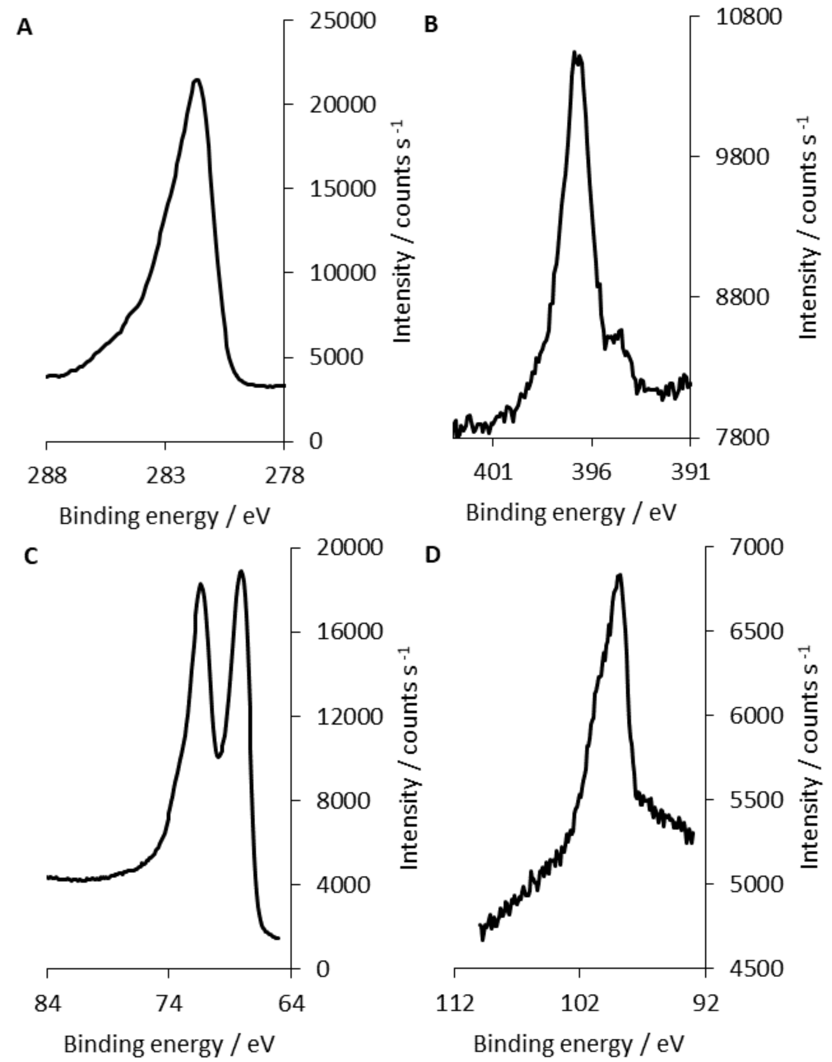

Figure 3A.10. XP spectra for sample two of five for the first five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

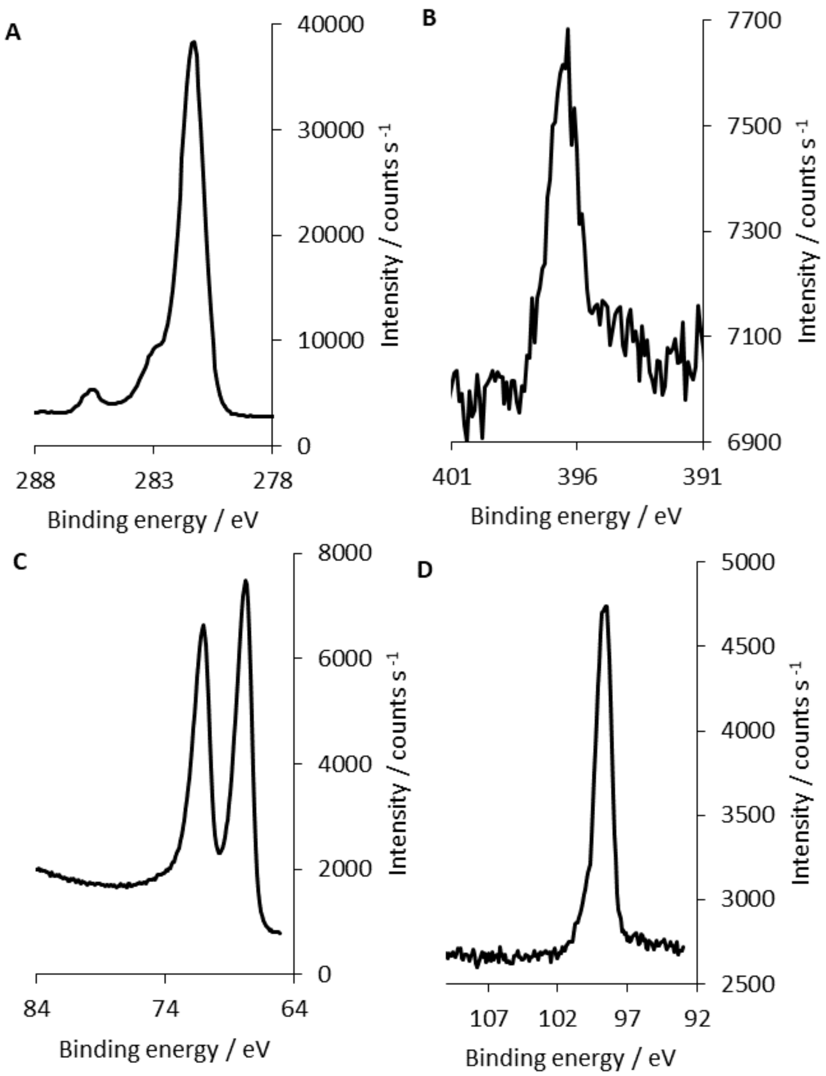

Figure 3A.11. XP spectra for sample three of five for the first five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

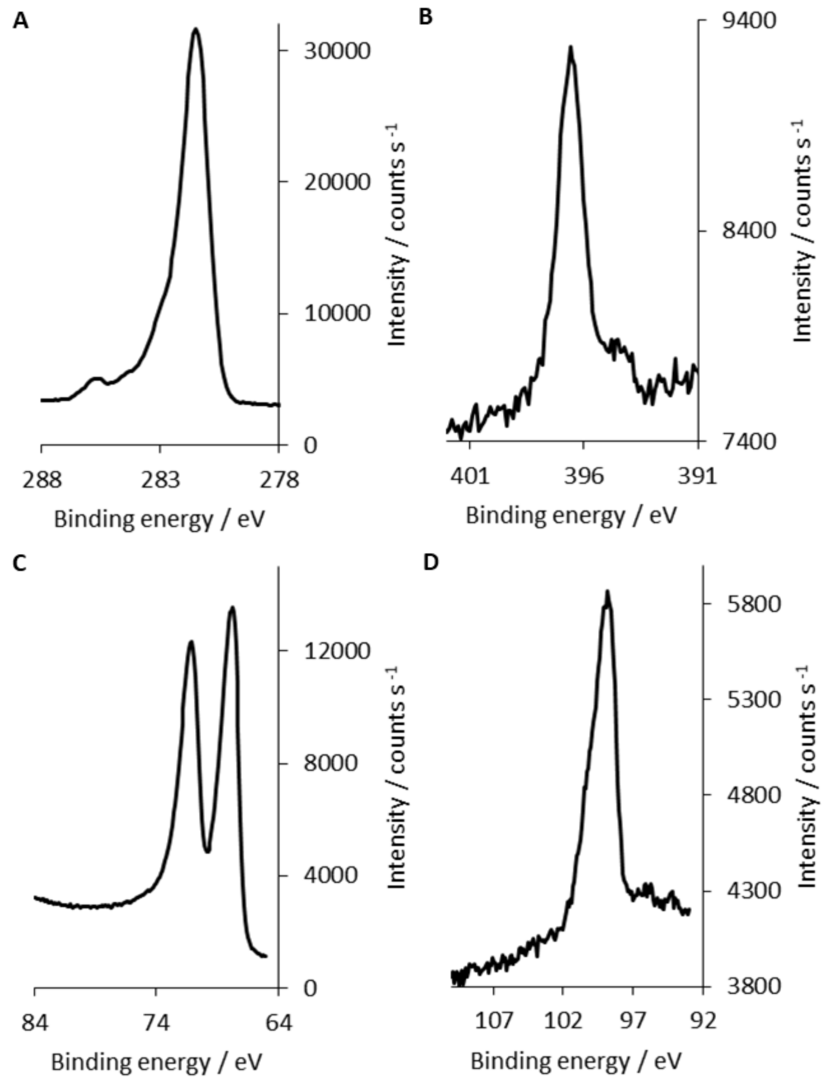

Figure 3A.12. XP spectra for sample four of five for the first five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

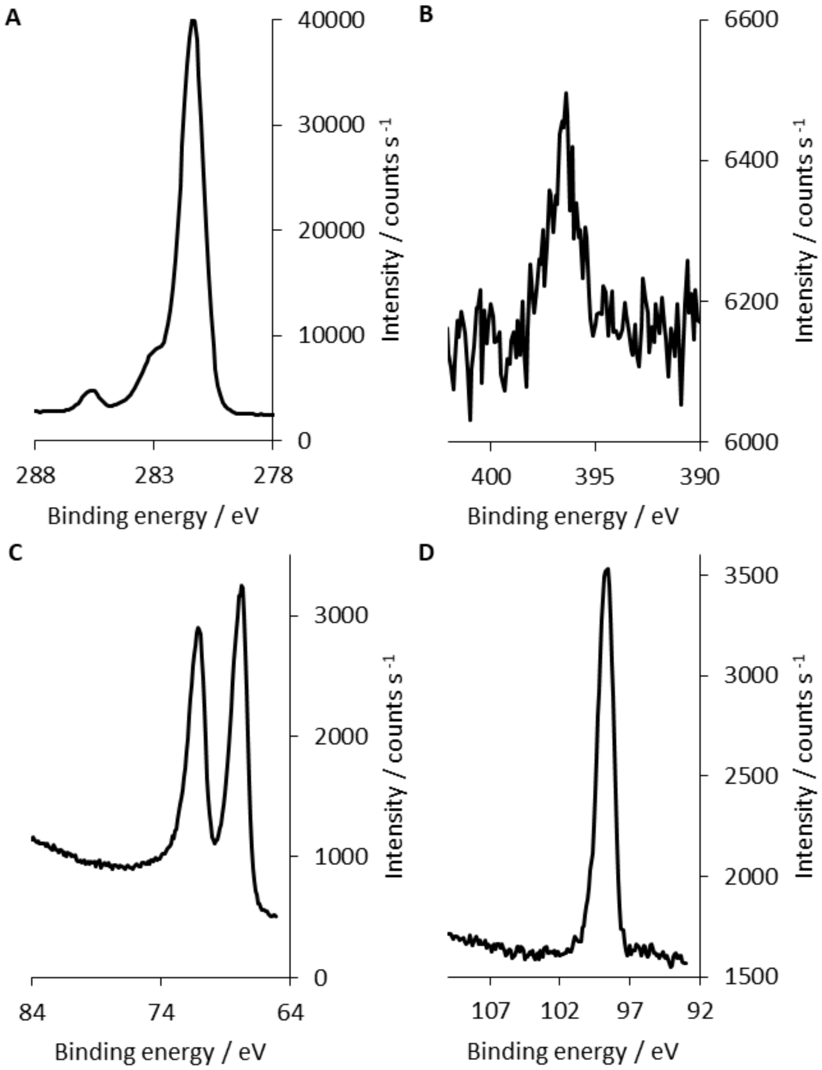

Figure 3A.13. XP spectra for sample five of five for the first five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

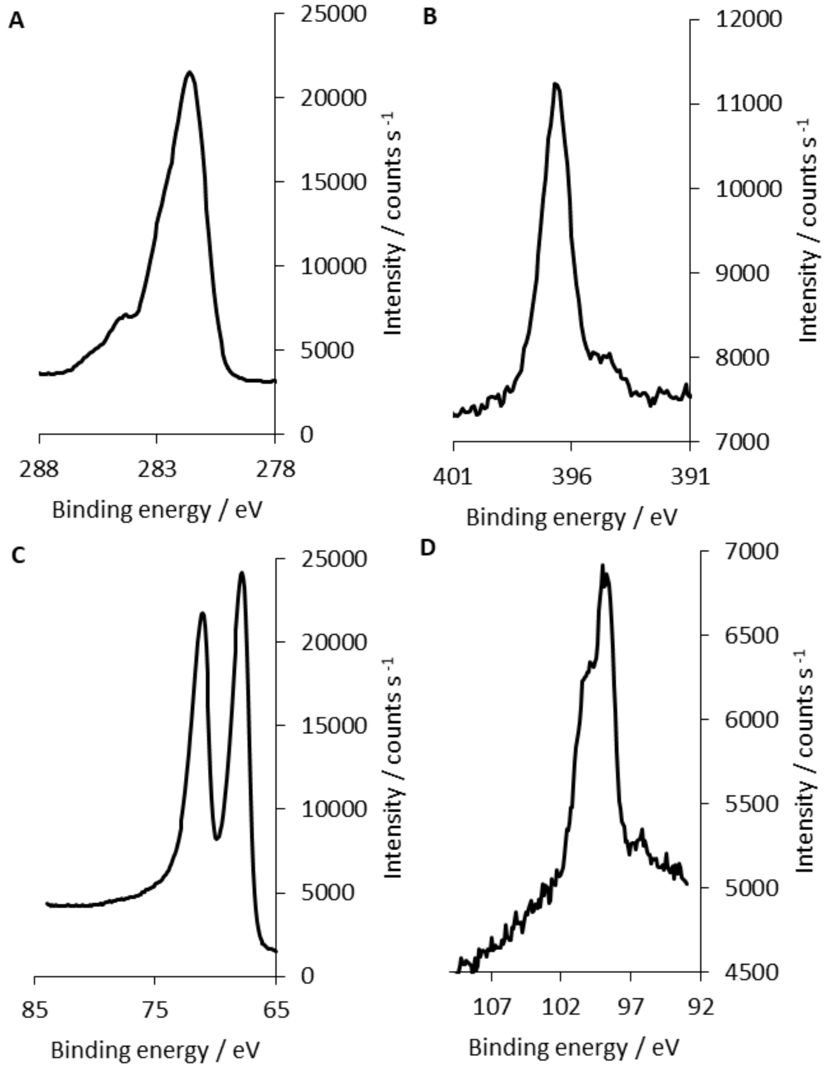

Figure 3A.14. XP spectra for sample one of five for the second five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

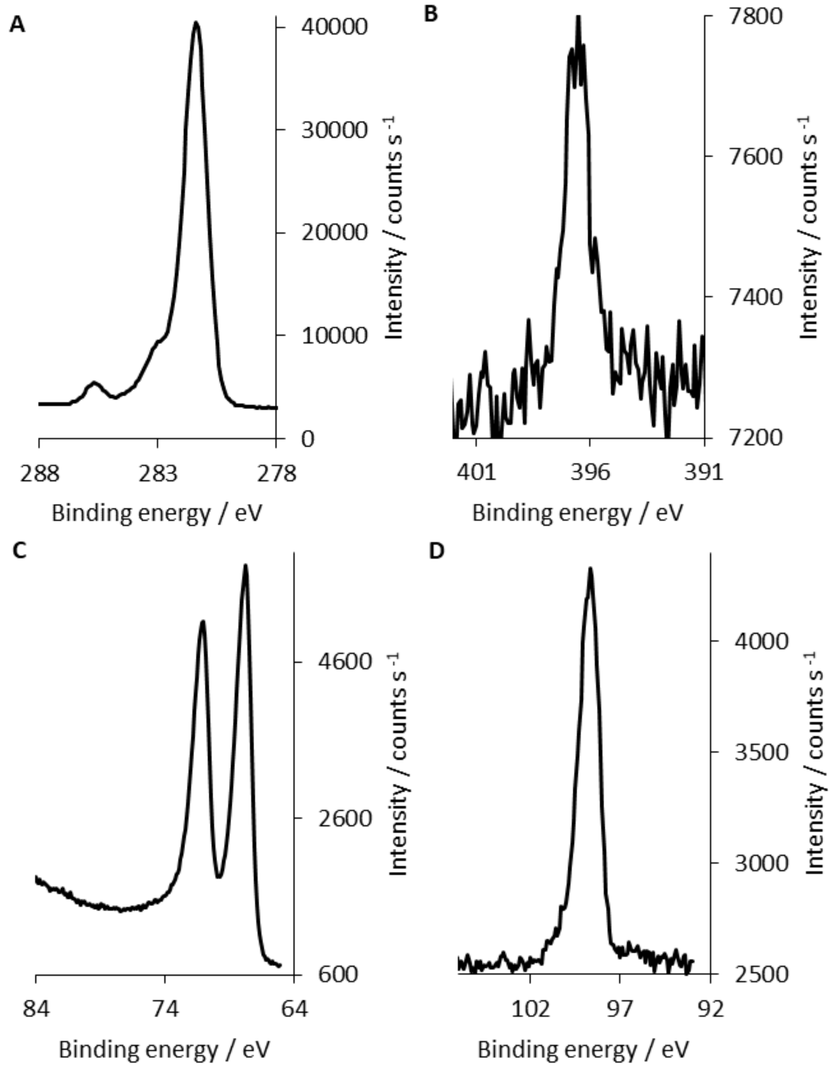

Figure 3A.15. XP spectra for sample two of five for the second five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

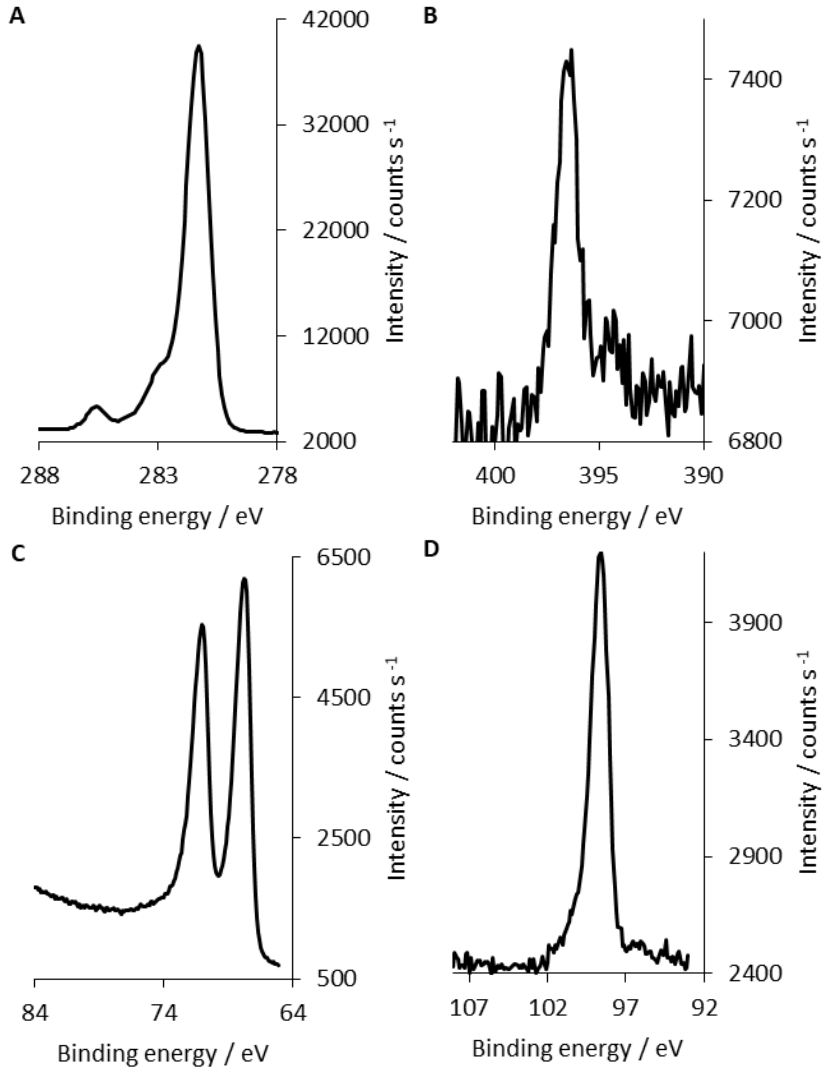

Figure 3A.16. XP spectra for sample three of five for the second five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

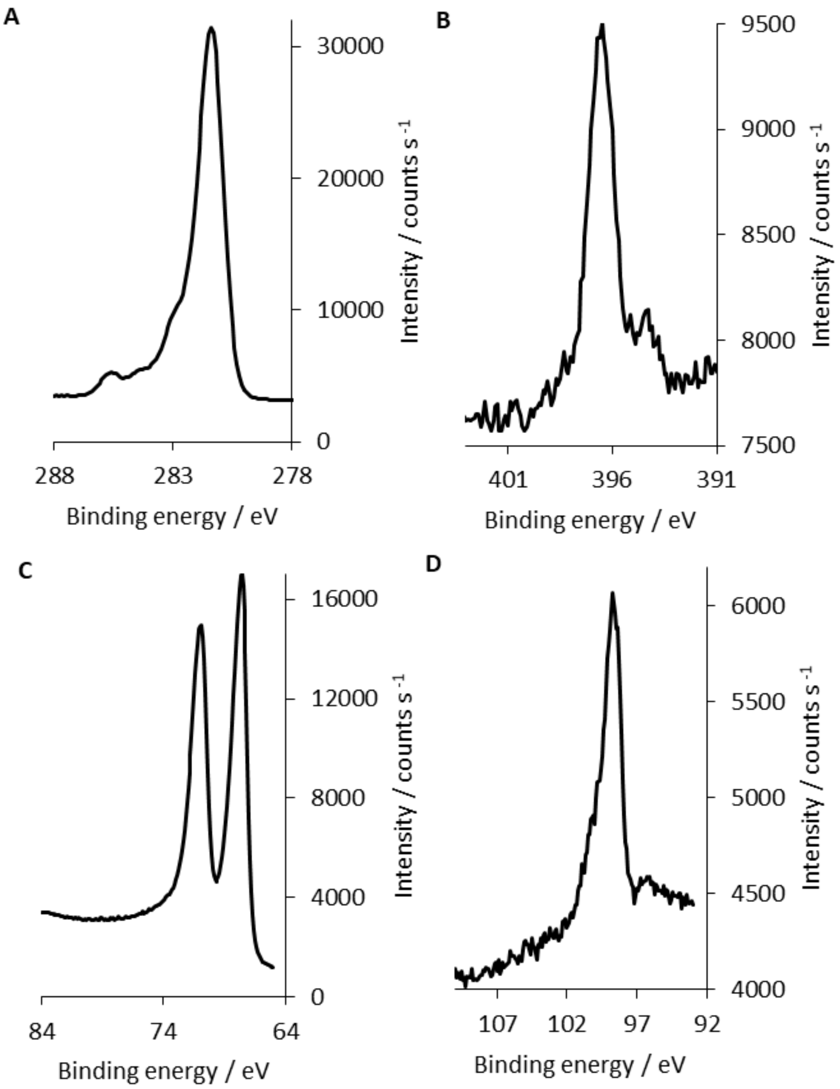

Figure 3A.17. XP spectra for sample four of five for the second five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

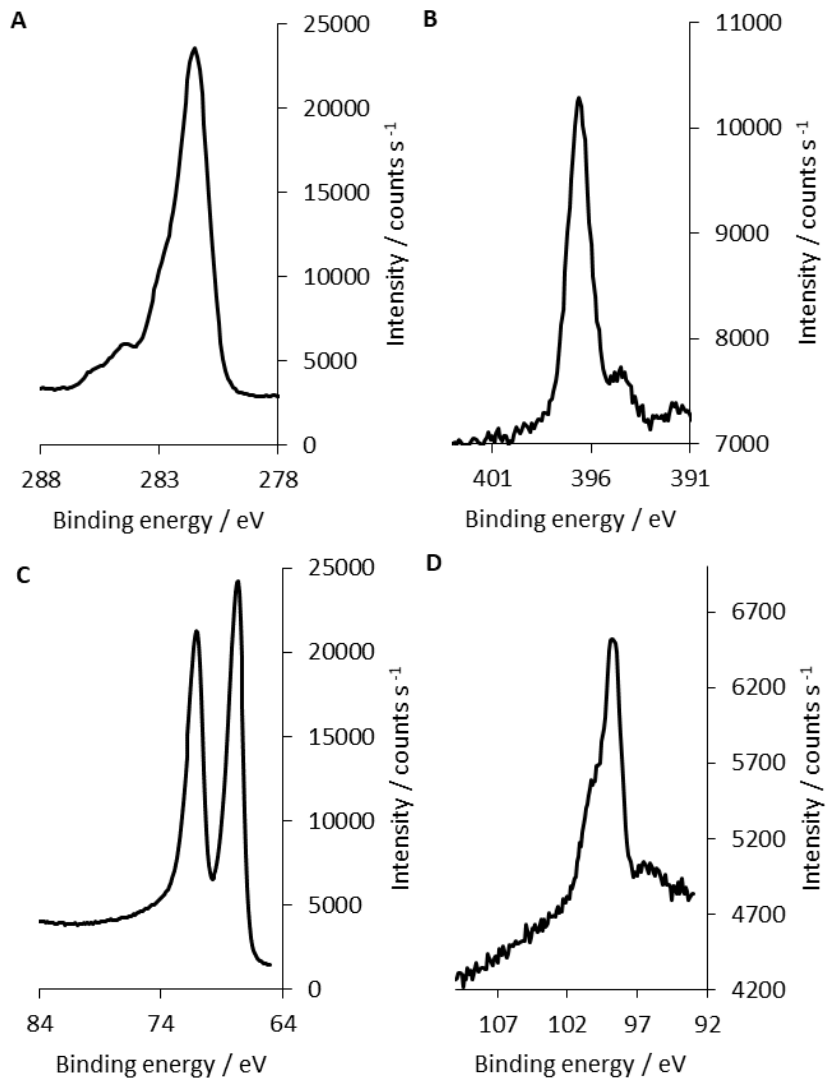

Figure 3A.18. XP spectra for sample five of five for the second five points surveyed for platinum/PVP nps supported using LB techniques upon a silica window (with one dipping of the substrate within the trough) for the following elements and bands: A) carbon 1s, B) nitrogen 1s, C) platinum 4f, and D) silicon 2p.

Table 3A.1. Tables to show platinum (Pt) coverage and preliminary values leading to calculation of these values. Platinum/silicon atomic ratio (Pt/Si At.%) values were calculated from fitting of spectra using Casa XPS (Chapter 2, Section 2.2.5.5)*, for three platinum/PVP LB deposited samples- two silicon wafer deposited sample with one and two layers- five data points, and silica window (single layer LB deposited) – ten data points.*

1 layer silicon wafer	**Pt/Si At.%**	**Pt/Si area ratio (1.d.p)**	**Pt coverage as cube / %**	**Pt coverage as spherical particle / %**
1	0.0	0.0	3	4
2	0.1	0.2	17	21
3	0.1	0.1	7	9

2 layer silicon wafer	**Pt/Si At.%**	**Pt/Si area ratio (1.d.p)**	**Pt coverage as cube / %**	**Pt coverage as spherical particle / %**
1	0.3	0.5	33	42
2	0.5	0.8	43	54
3	0.5	0.8	44	55

Silica window	**Pt/Si At.%**	**Pt/Si area ratio (1.d.p)**	**Pt coverage as cube / %**	**Pt coverage as spherical particle / %**
1	0.3	0.4	30	38
2	0.5	0.8	46	57
3	0.3	0.6	35	44
4	0.6	0.9	48	60
5	0.2	0.3	21	26
6	0.8	1.3	56	69
7	0.3	0.5	31	39
8	0.3	0.5	32	39
9	0.6	1.0	49	61
10	0.6	1.0	50	62

Pt/PVP np and polyvinylpyrrolidone in ethanol concentration calculation

Calculation was undertaken to determine, for samples prepared for ultraviolet-visible (UV-vis) spectroscopic analysis at a concentration of 1 mg mL^{-1} in ethanol, if the total concentration of polyvinylpyrrolidone was similar in the pure polyvinylpyrrolidone samples compared to that of the platinum/PVP np samples.

In the nanoparticle synthesis 0.1 g of chloroplatinic acid hexahydrate was used, and so the percentage by weight of platinum in the start material was;

(195.084 g mol^{-1}/517.90 g mol^{-1}) x 100=37.67%

So in 0.1 g, the mass of platinum present is;

0.1 g x (37.67/100)=0.03767 g (4.s.f)

To the reaction mixture 0.44 g of polyvinylpyrrolidone was added. If we assume all of the polyvinylpyrrolidone is consumed and the nanoparticle product is therefore composed of the total start mass of each component then the final product weight is:

0.03767 g + 0.44 g = 0.4777 g (4.s.f.).

The percentage of polyvinylpyrrolidone in the product is therefore given by:

(0.44 g/0.4777 g) x 100 = 92.11%

So for the 1mg mL^{-1} nanoparticle sample the concentration of polyvinylpyrrolidone in ethanol is 0.9211 mg mL^{-1}.

For a polyvinylpyrrolidone concentration of 1 mg mL^{-1} the percentage difference, of polyvinylpyrrolidone concentration, between the two samples is 4% as given below.

(1 mg mL^{-1}-0.9211 mg mL^{-1}) / (1 mg mL^{-1} + 0.9211 mg mL^{-1}) = 4%.

Hence the difference in polyvinylpyrrolidone concentration is suitably small, and given the magnitude in the difference of the absorbance spectra is unlikely to contribute to the differences observed.

Polyvinylpyrrolidone characterisation and purification: Nuclear magnetic resonance (NMR) spectroscopy

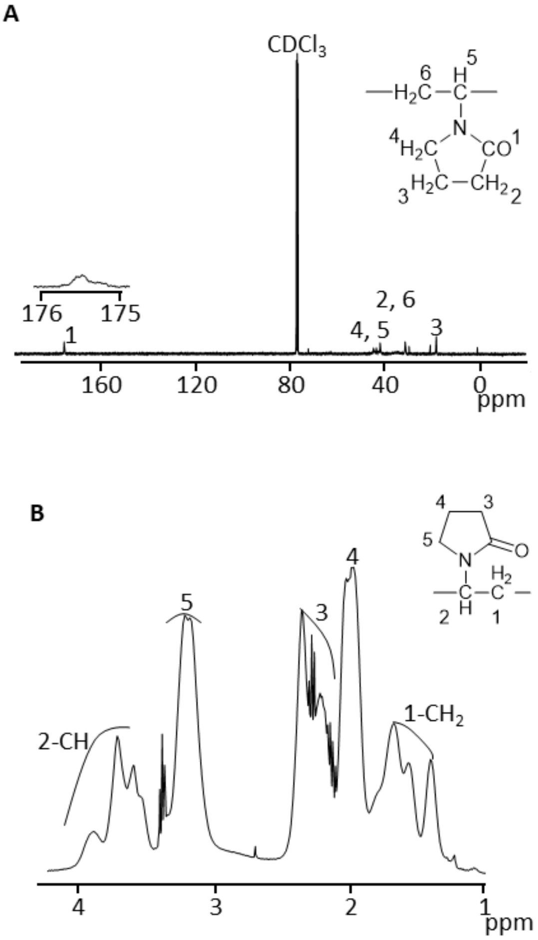

Figure 3A.19. A) ^{13}C, and B) ^{1}H NMR spectra for polyvinylpyrrolidone after Soxhlet purification with sample collected from the dialysis tube.

Table 3A.2. Literature values for ^{13}C NMR spectroscopy of polyvinylpyrrolidone.[2]

Shift / ppm-coupling	**Assignment**
18.4-s	3-CH_2
30.8-32.3-s	2-CH_2
32.3-38.0-s	6-CH_2
41.5-43.5-m	4-CH_2
43.5-46.0-m	5-CH
175.0-175.9-s	1-CO

Table 3A.3. Assignment of ^{13}C NMR spectra (Figure 3A.19 A) for polyvinylpyrrolidone after Soxhlet purification with sample collected from a dialysis bag.

Shift / ppm-coupling	**Integration**	**Assignment**
18.3-s	1	3-CH_2
31.4-s	1	2-CH_2
42.1-43.5	1	4-CH_2
44.8	1	5-CH
175.4-s	1	1-CO

Table 3A.4. Literature values for ^{1}H NMR spectroscopy of polyvinylpyrrolidone.[2]

Shift / ppm	**Assignment**
1.4-1.7	1-CH_2
2.0	4-CH_2
2.2-2.4	3-CH_2
3.25	5-CH_2
3.4-3.9	2-CH

Table 3A.5. Assignment of ^{1}H NMR spectra (Figure 3A.19 B) for polyvinylpyrrolidone after Soxhlet purification with sample collected from a dialysis bag. N/A means no assignment could be made for the peak listed.

Shift / ppm-coupling	**Integration**	**Assignment**
1.6-dd	2	1-CH_2
2.0-m	2	4-CH_2
2.2-2.4 tq,s	2	3-CH_2
2.6-s	N/A	N/A
3.2-3.3 s	2	5-CH_2
3.7-s	1	2-CH

Bibliography

(1) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. Langmuir−Blodgett Silver Nanowire Monolayers for Molecular Sensing Using Surface-Enhanced Raman Spectroscopy. *Nano Lett.* **2003**, *3* (9), 1229–1233.

(2) Dutta, K.; Brar, A. S. Poly(vinylpyrrolidone): Configurational Assignments by One- and Two-Dimensional NMR Spectroscopy. *J. Polym. Sci. Part Polym. Chem.* **1999**, *37* (21), 3922–3928.