Synthesis of Yellow-Emitting Platinum Nanoclusters by Ligand Etching

Xavier Le Guével,† Vanessa Trouillet,‡ Christian Spies, § Gregor Jung, § and Marc Schneider*,†

†Pharmaceutical Nanotechnology, Saarland University, Saarbrücken, Germany
‡Institute for Applied Materials, KIT-Campus North, Karlsruhe, Germany
§ Department of Biophysical Chemistry, Saarland University, Saarbrücken, Germany

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Indranath Chakraborty
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Introduction

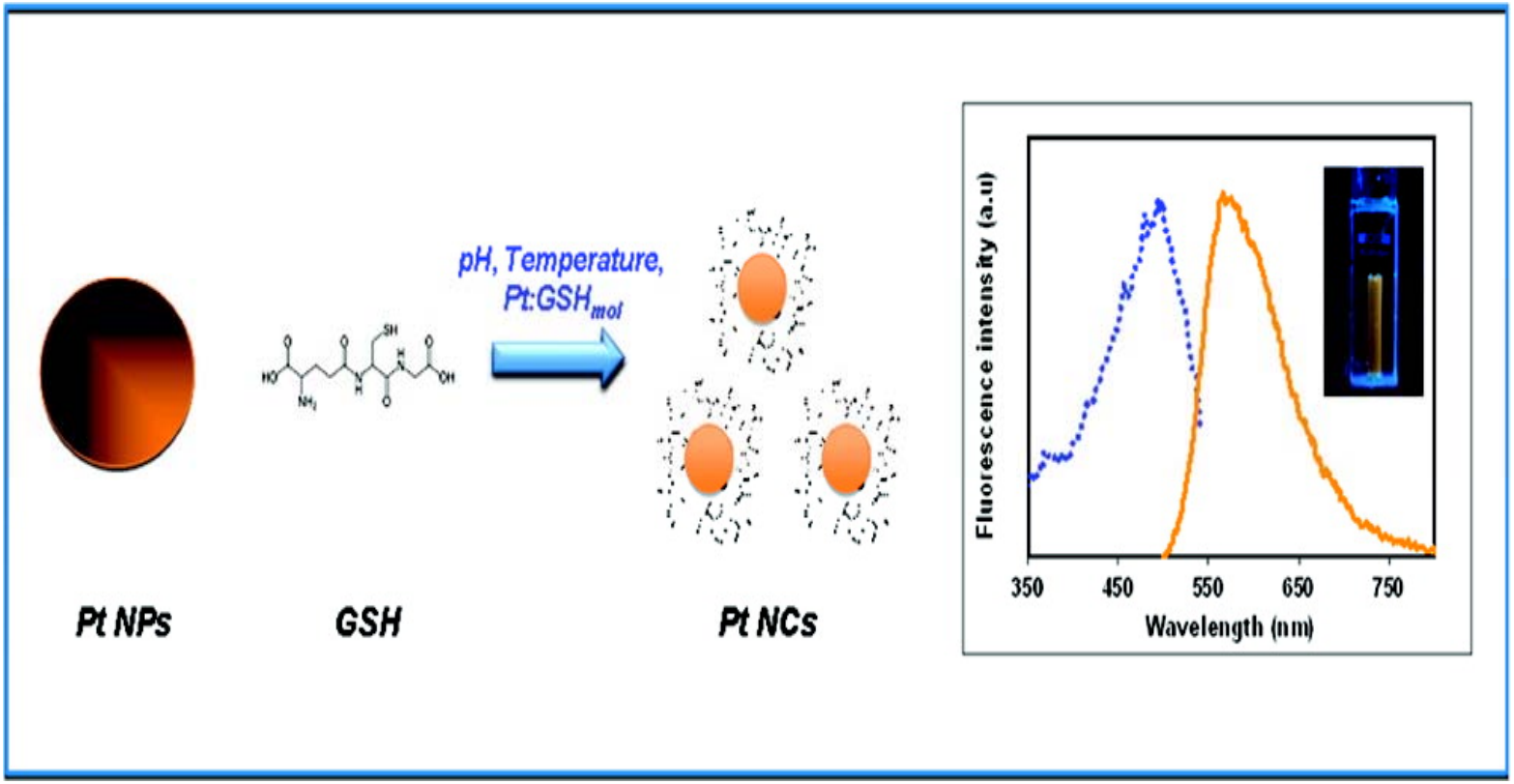
Noble metal nanoclusters exhibit unique properties compared to their homologues on the nanometric scale (size >2 nm) such as fluorescence, chirality, or magnetism.

The strong quantum size effect and the absence of the surface plasmon band leads to interesting molecule-like properties such as strong fluorescence, allowing one to obtain NCs with distinct optical features.

Platinum (another noble metal) particles are already developed for their catalytic activity, but it is only recently that two research groups demonstrated the molecular-like properties of blue-emitting platinum NCs stabilized by a dendrimerand by dimethylformamide.

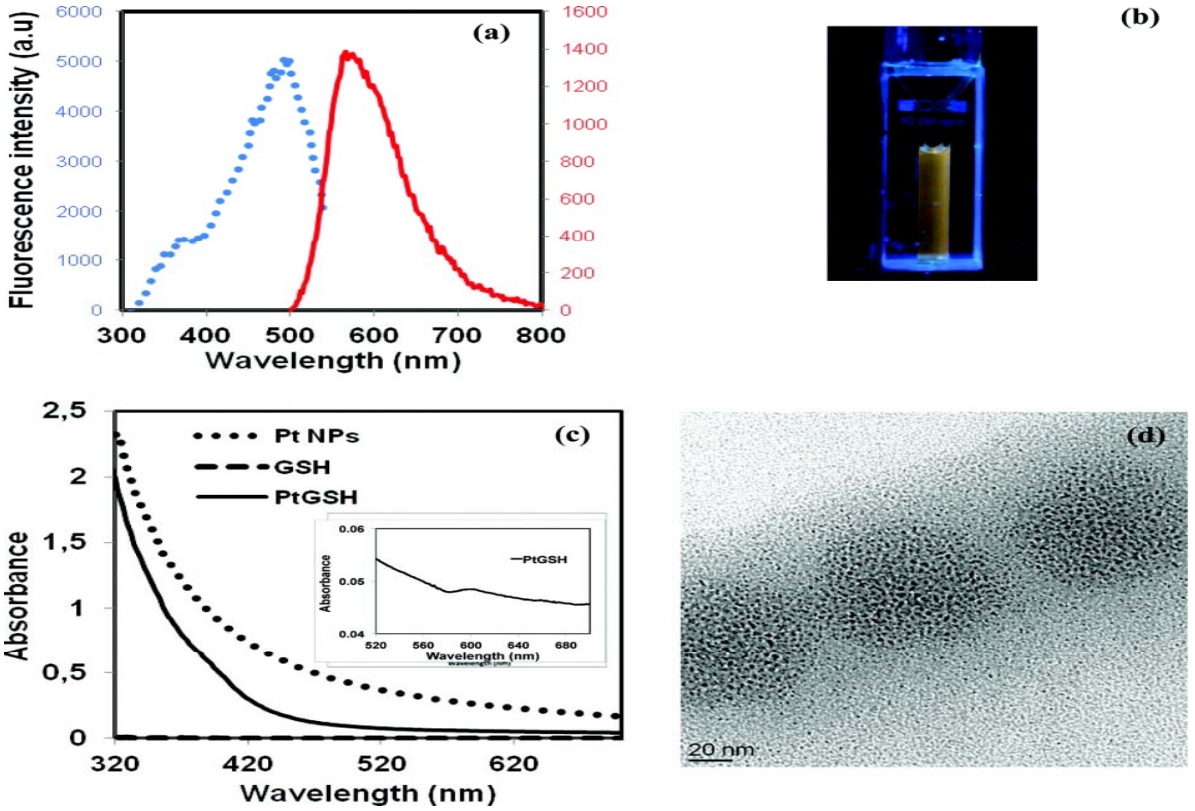
Here the synthesis of stable platinum NCs (PtGSHs) by ligand etching prcess has done and its optical and spectroscopic investigations were performed

Experimental overview



Optimum temperature is 65^{o}C

Results and Discussion



(a) Excitation (dashed line) and emission (solid line) spectra of the yellow-emitting NCs PtGSH after subtraction of GSH autofluorescence. (b) PtGSH under UV irradiation (λ = 366 nm). (c) Absorbance profile of platinum particles (Pt NPs), platinum clusters (PtGSH), and the etching ligand GSH. (d) Microscopy image (TEM) of PtGSH.

Results and Discussion

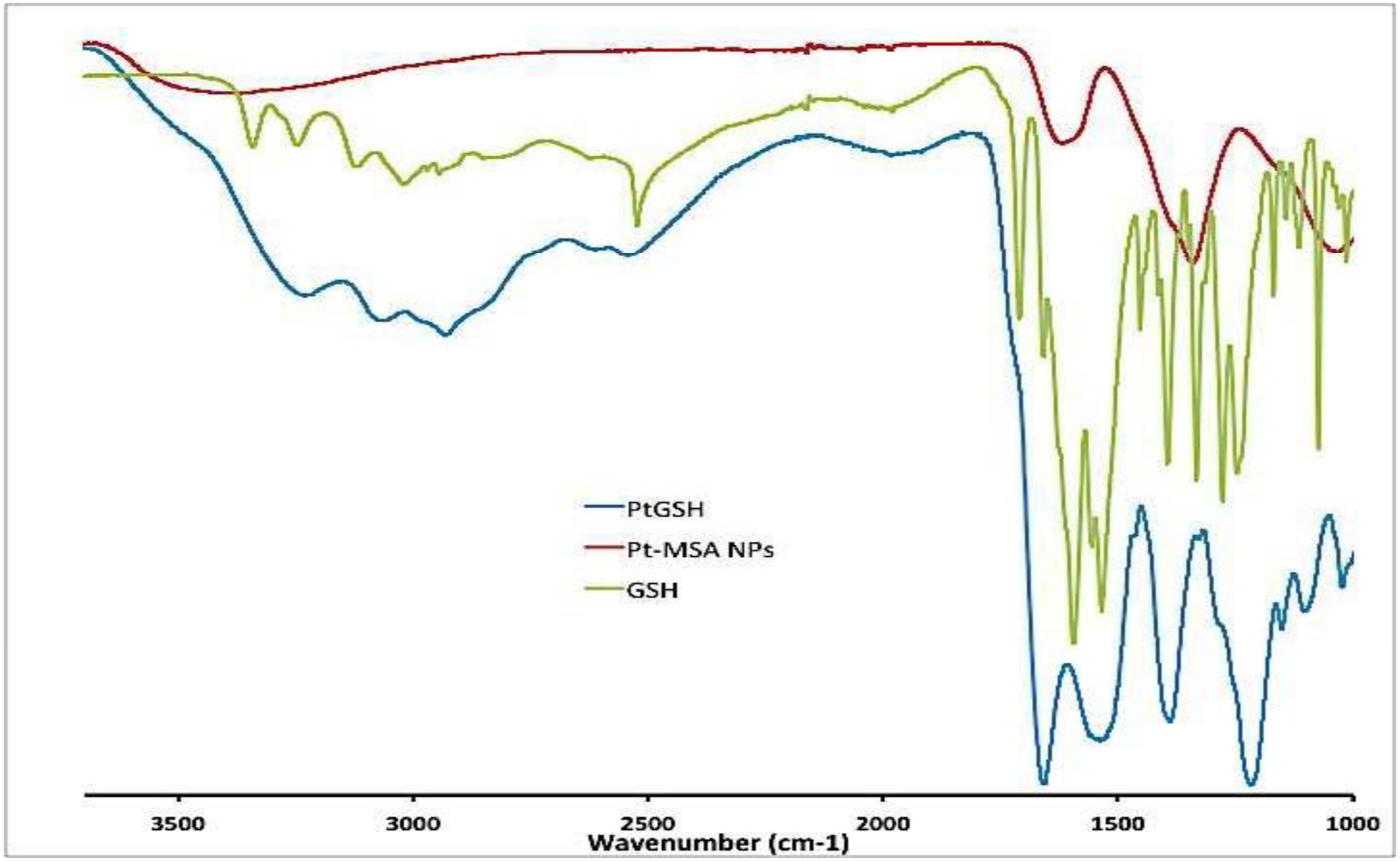
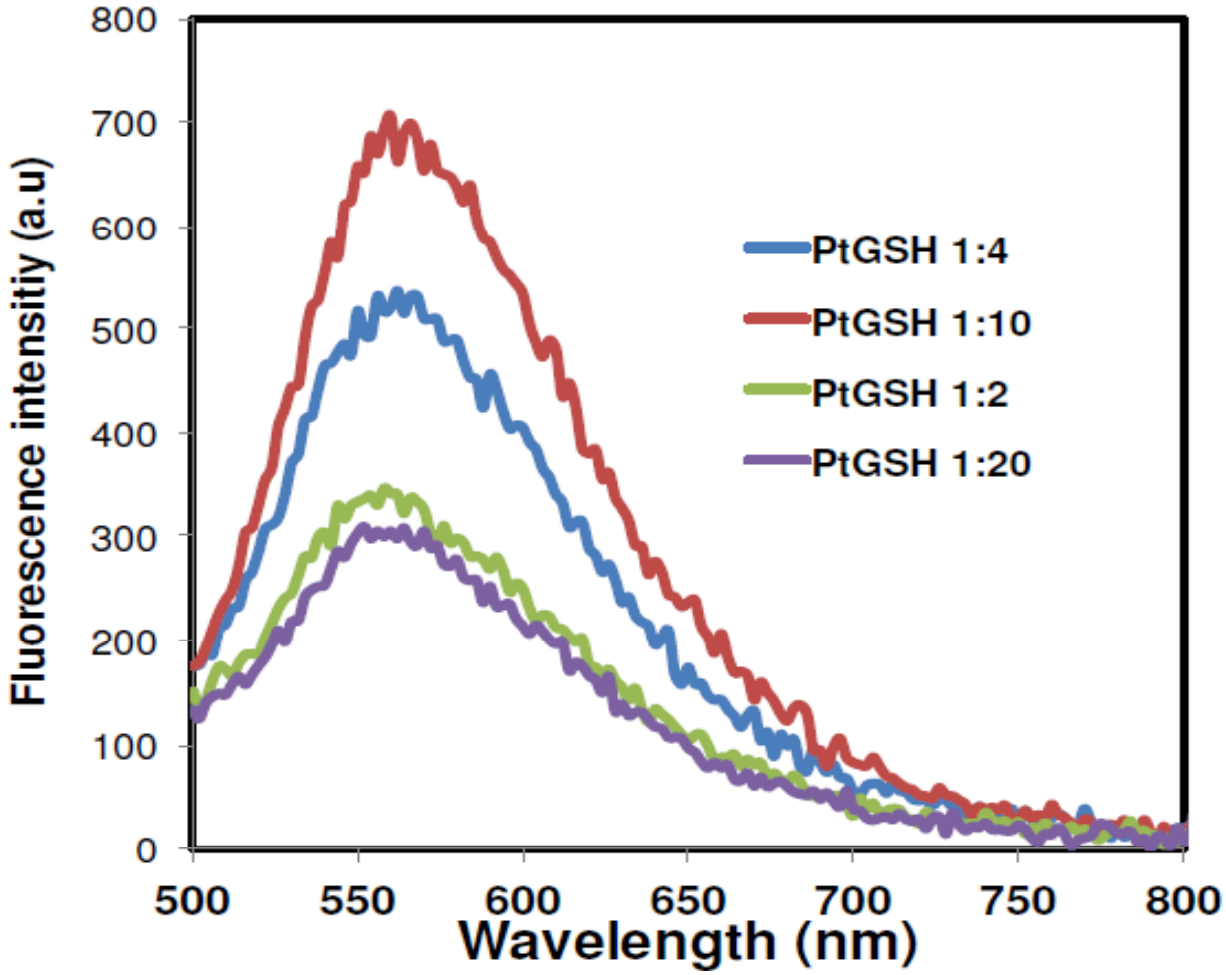


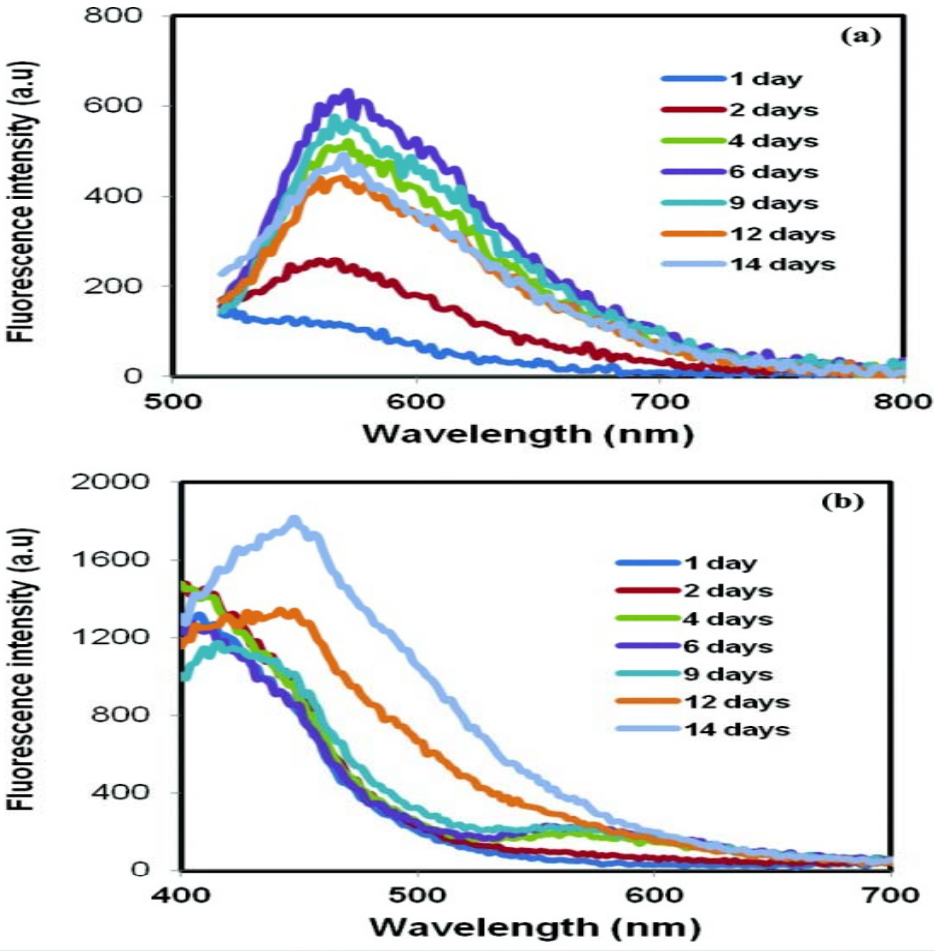
Figure S7. Infrared spectra of PtGSH, Pt-MSA NPs and GSH between 1000 and 3800 cm-1. Results indicate the presence of the carboxyl groups (1720 cm-1) of GSH on PtGSH sample. The broader band at 2520 cm-1 for PtGSH compared to GSH suggests the covalent interaction between the thiol groups of GSH and the surface of the platinum clusters.

Results and Discussion



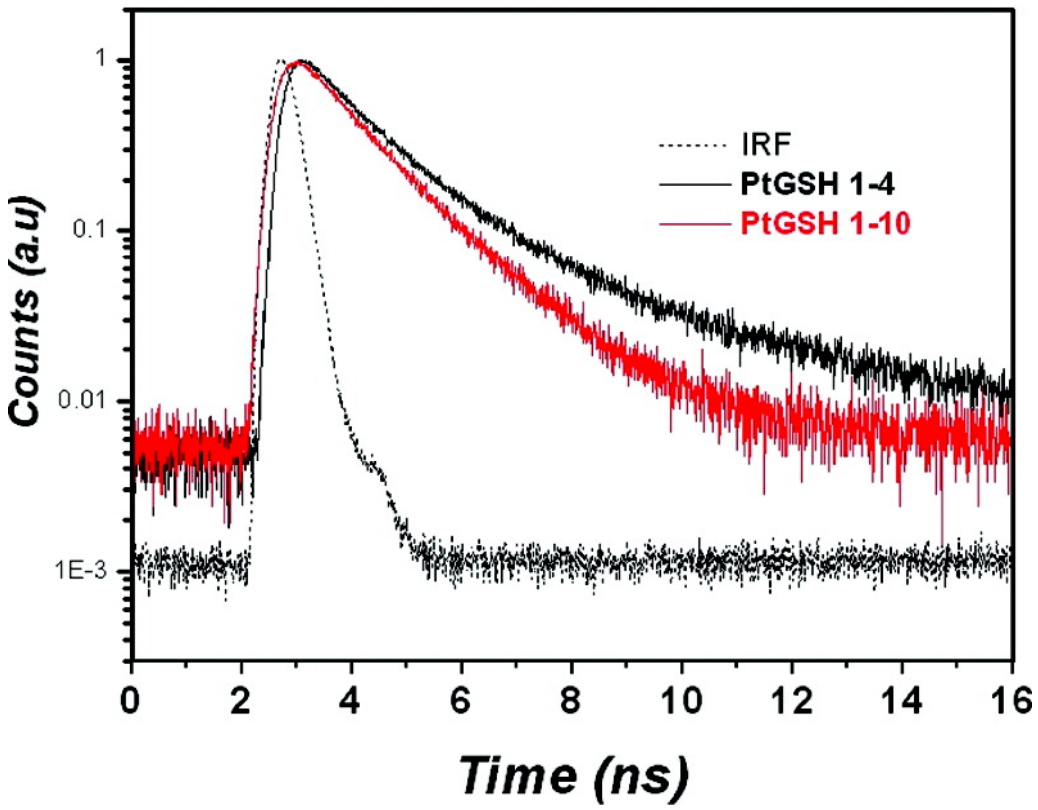
Fluorescence emission spectra of PtGSH prepared at different weight ratios Pt:GSH after 6 days of etching process. (λexc. = 460 nm; gain=100).

Results and Discussion



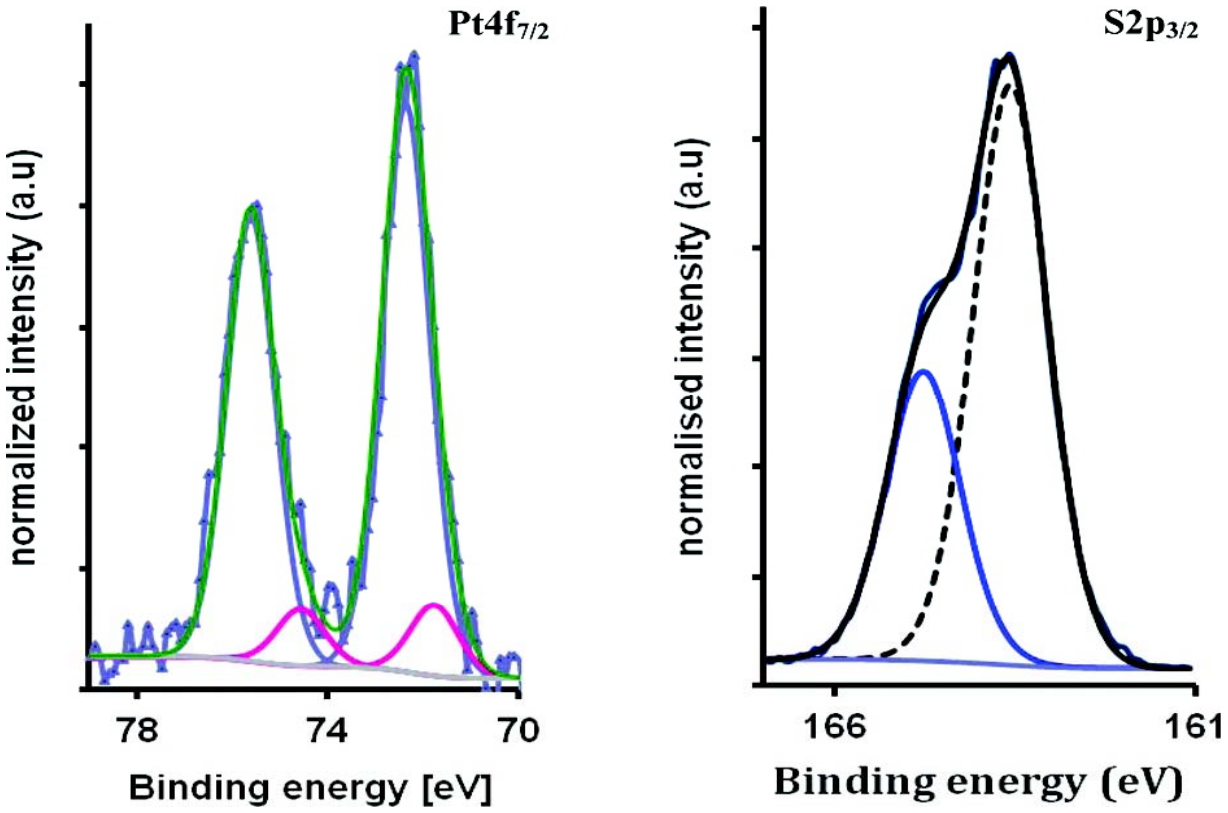
Fluorescence emission spectra of PtGSH at different etching times upon excitation at λ = 480 nm (a) and λ = 360 nm (b). Data show the growth of a yellow-emitting species up to 6 days following by the emergence of a blue-emitting species for a long etching process.

Results and Discussion



Lifetime decay of PtGSH prepared at two different weight ratios: Pt:GSH = 1:4 (black line) and 1:10 (red line). Samples were measured upon an excitation at 470 nm and fluorescence was collected at 585 ± 25 nm. Lifetime components for PtGSH 1–4: τ1 = 1.02 ns (85%), τ2 = 3.4 ns (15%); and for PtGSH 1–10: τ1 = 1.04 ns (85%), τ2 = 2.01 (15%).

Results and Discussion



XPS spectra. (a) Pt 4f7/2 of PtGSH shows two peaks, one peak at 72.4 eV (green curve) and the other at 71.6 eV (pink curve), which are attributed to Pt(I) (90%) and Pt (0) (10%), respectively. (b) S 2p3/2 confirms the presence of platinum bound to sulfur (blue curve) with a peak at 163.3 eV.

Summary and Conclusion

In summary, the synthesis of yellow-emitting platinum NCs by interfacial synthesis has been achieved.

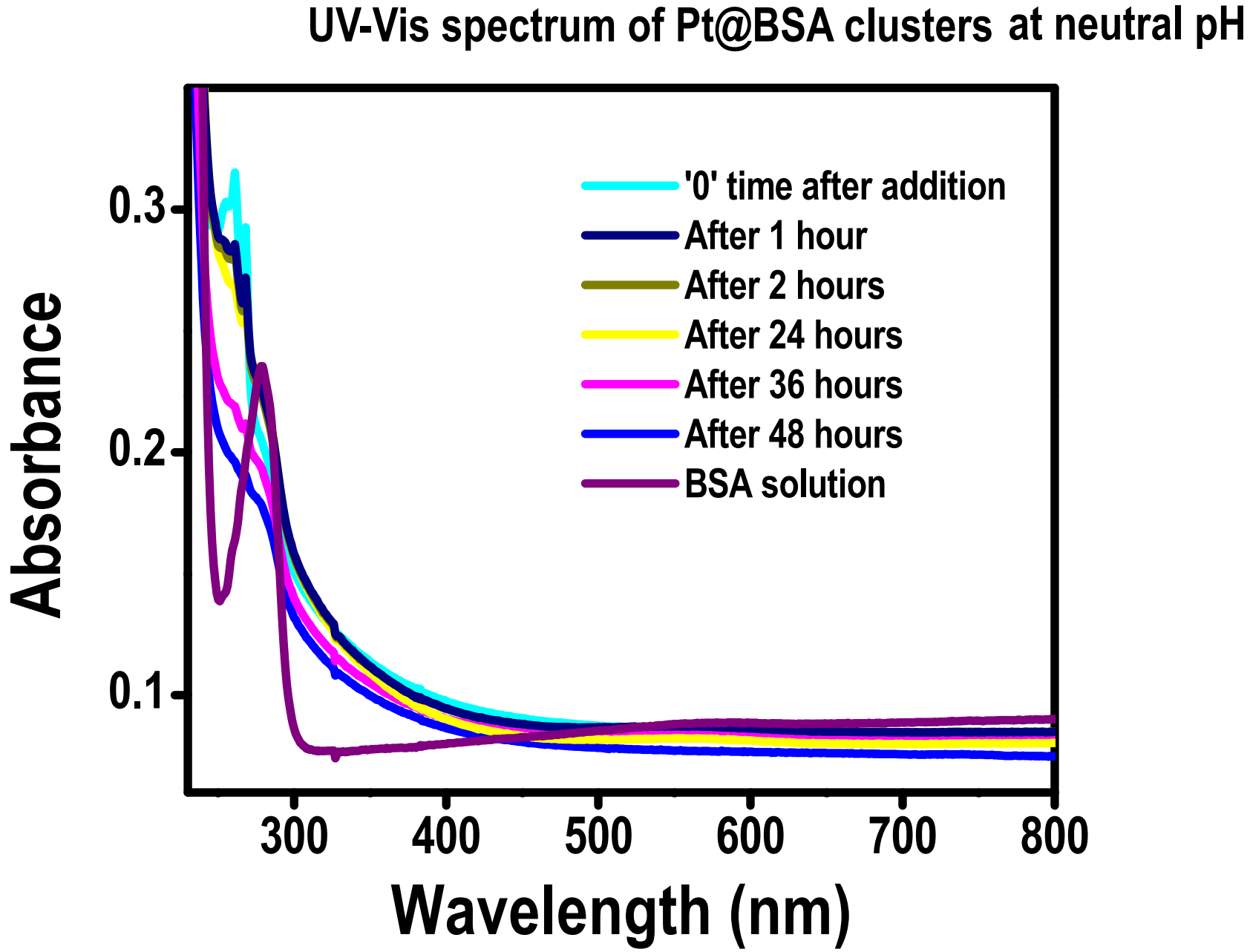
Compared to gold and silver NCs protected by GSH, platinum NCs are produced with slower kinetics of etching without the formation of red-NIR emitting species

These clusters are partially bound to GSH and mainly in the oxidation state I (Pt(I) = 90%)

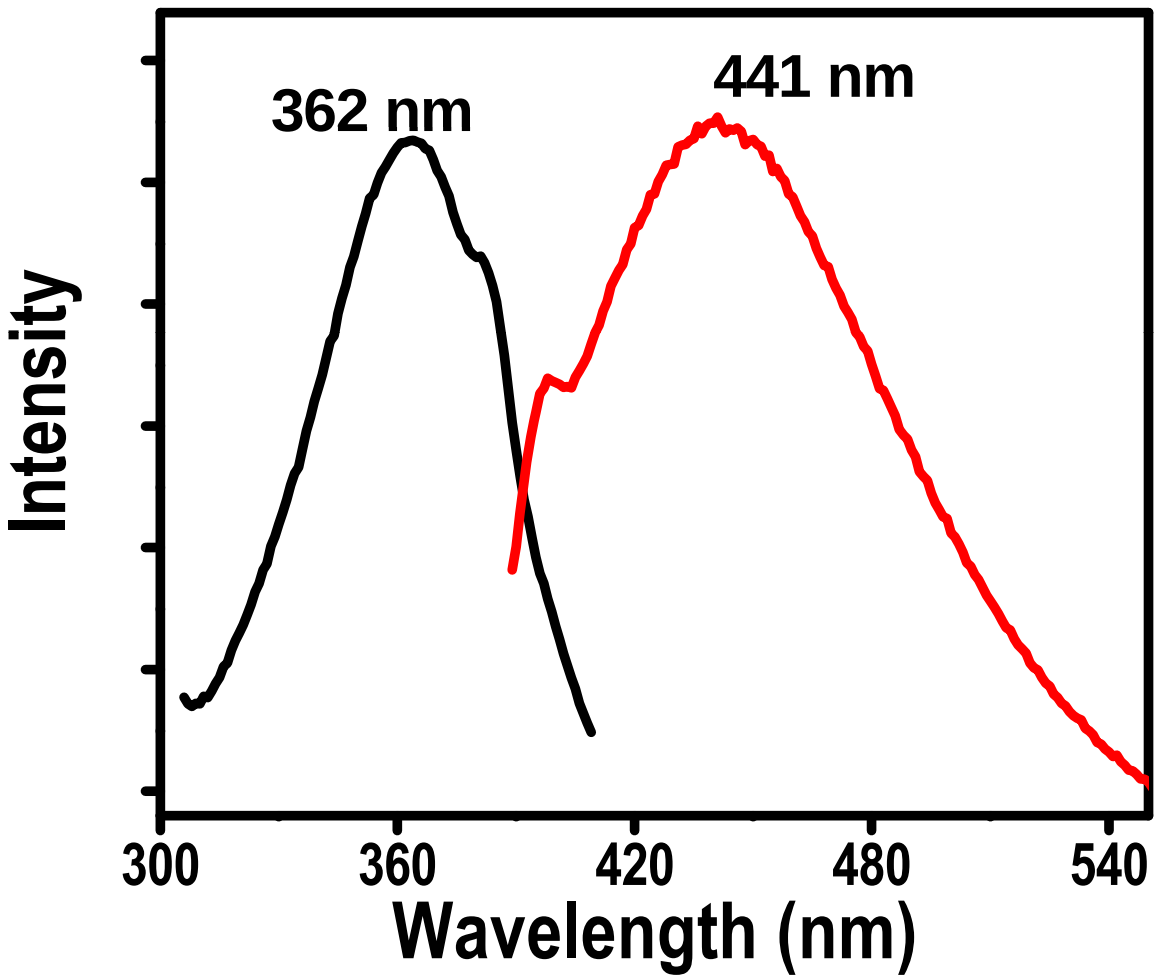
A longer etching process at high temperature involves the formation of blue emitting species accompanied by the degradation of the yellow emitting species.

Synthesis of Pt@BSA clusters at room temperature by interfacial etching using Pt@GSH nanoparticles

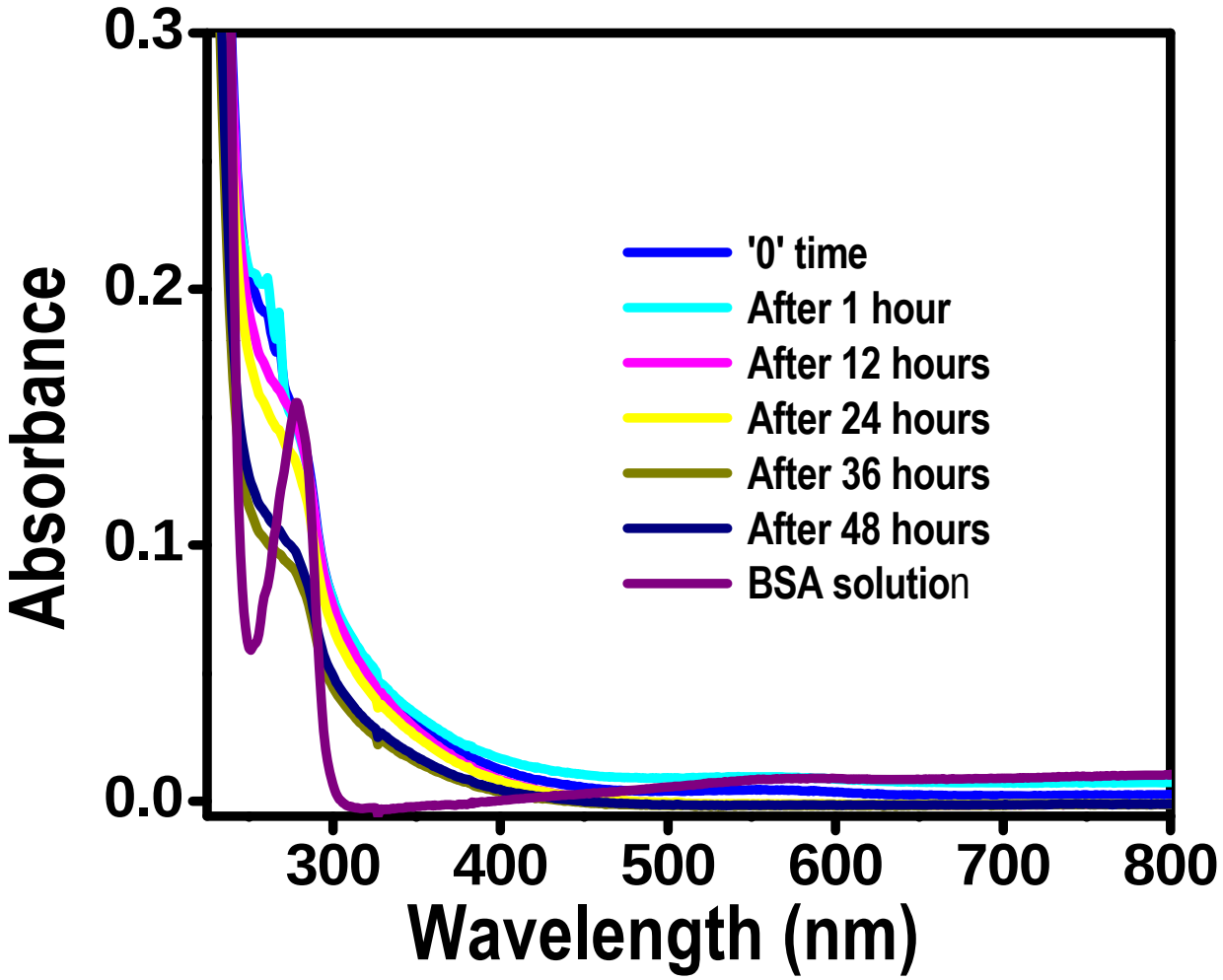
An extension of work by Mr. Balagunu (2007)

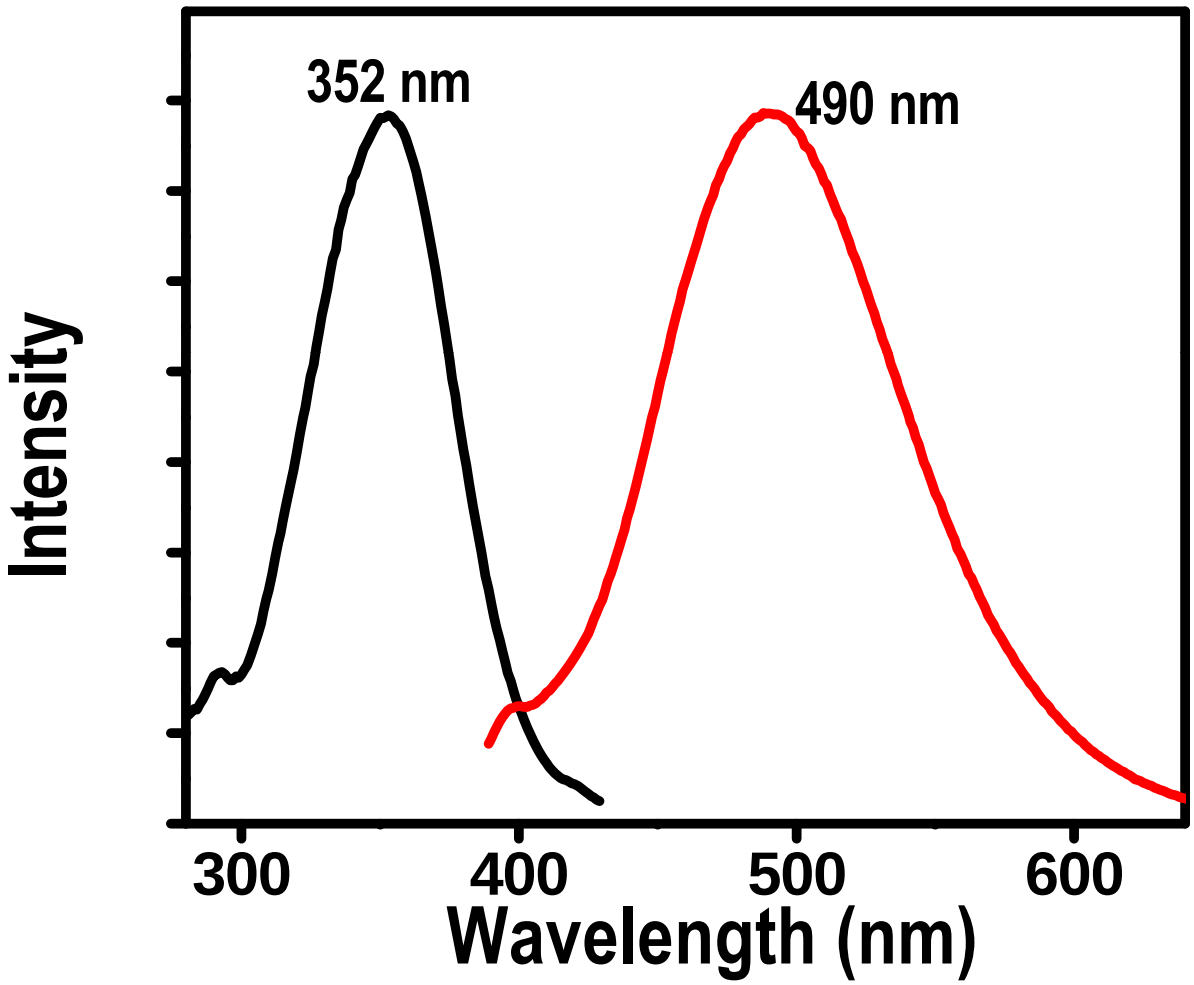

UV-Vis spectrum of Pt@BSA clusters at neutral pH
Absorbance
0.3
0.2
0.1
300
400
500
600
700
800
Wavelength (nm)
'0' time after addition
After 1 hour
After 2 hours
After 24 hours
After 36 hours
After 48 hours
BSA solution

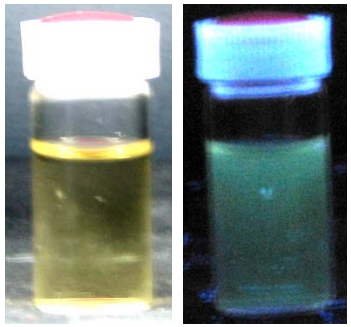
Fluorescence spectrum of Pt@BSA clusters



Pt@BSA cluster at pH 10

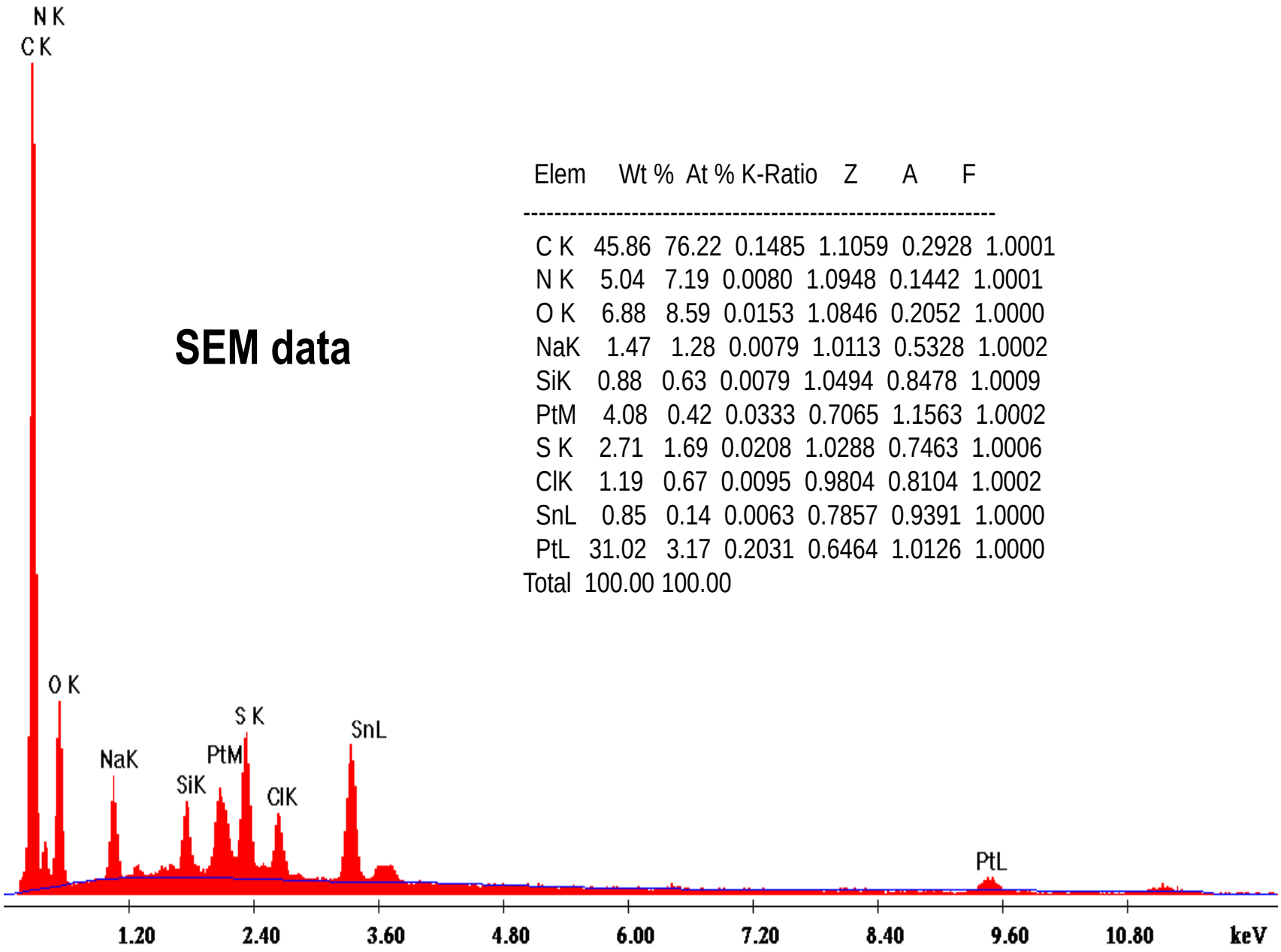


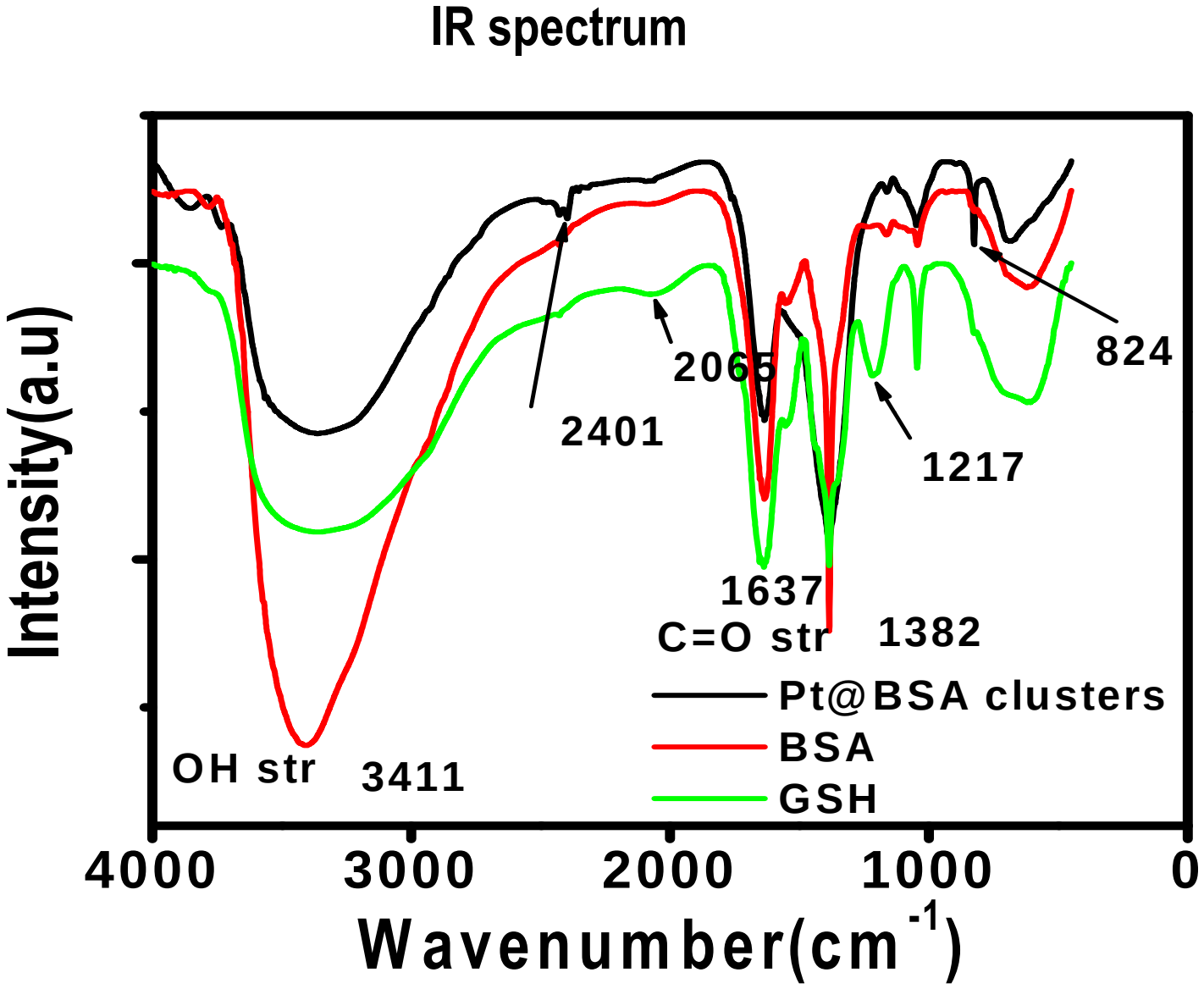

352 nm
490 nm
Intensity
300
400
500
600
Wavelength (nm)

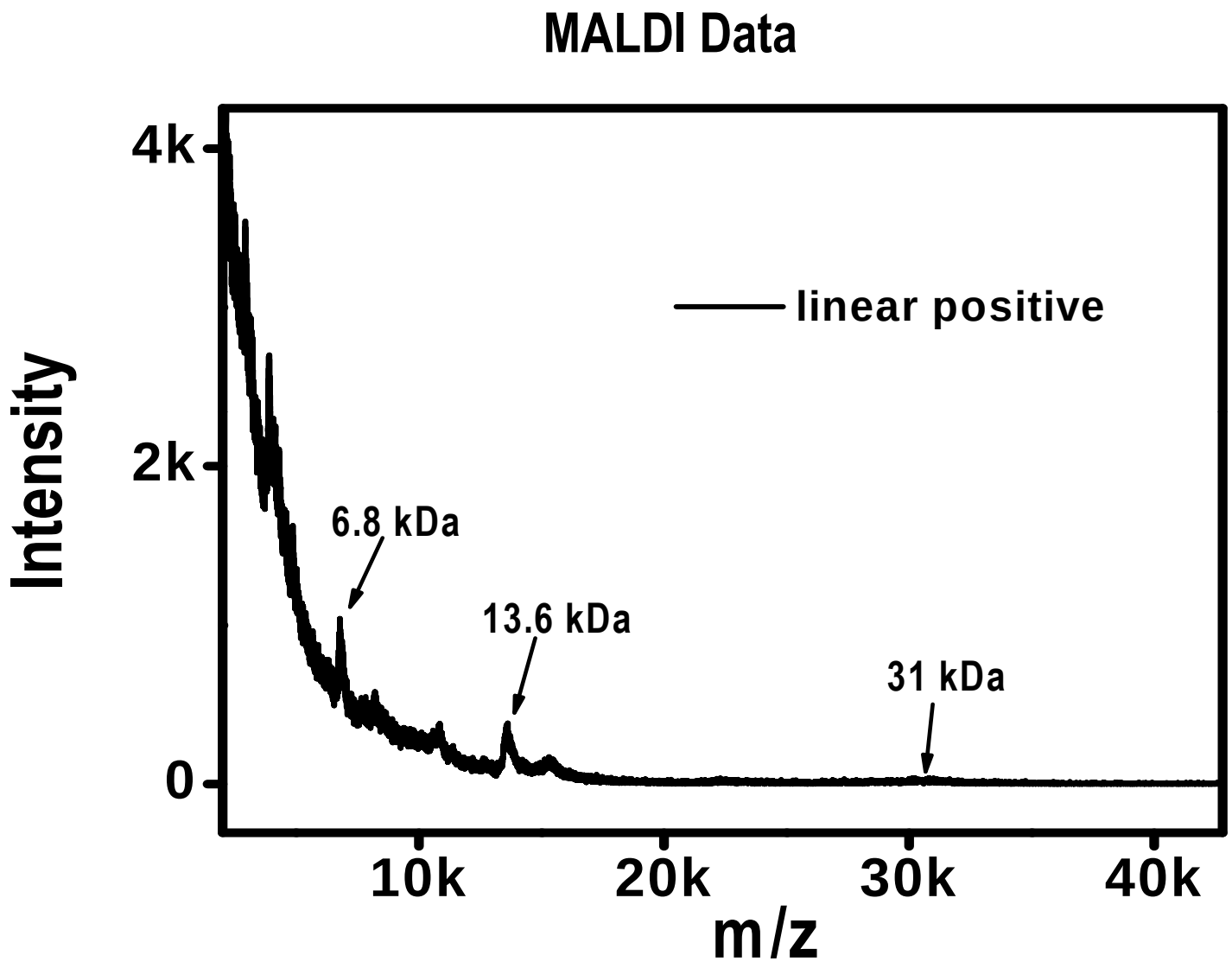


SEM data

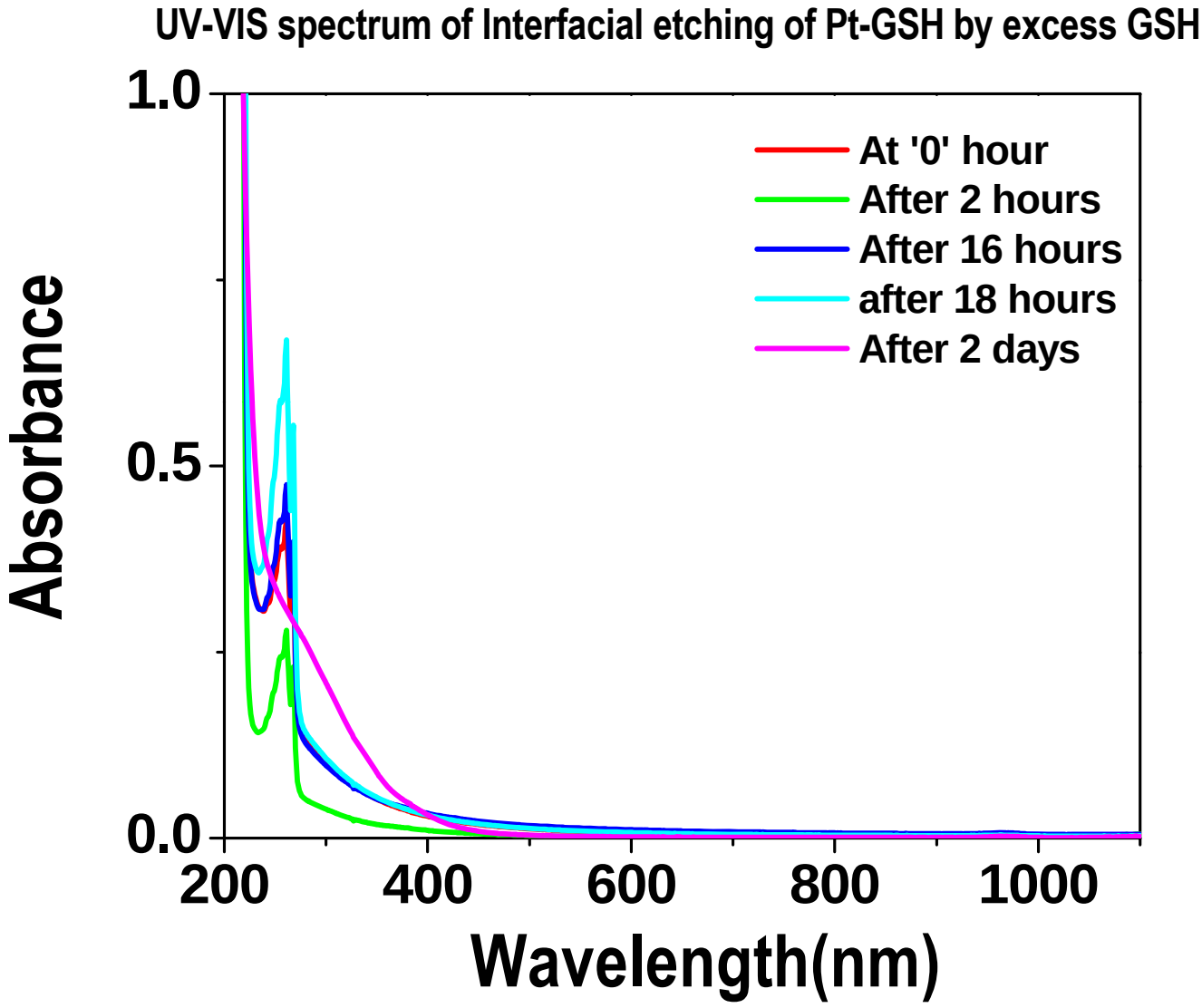
Elem	Wt %	At %	K-Ratio	Z	A	F
C K	45.86	76.22	0.1485	1.1059	0.2928	1.0001
N K	5.04	7.19	0.0080	1.0948	0.1442	1.0001
O K	6.88	8.59	0.0153	1.0846	0.2052	1.0000
NaK	1.47	1.28	0.0079	1.0113	0.5328	1.0002
SiK	0.88	0.63	0.0079	1.0494	0.8478	1.0009
PtM	4.08	0.42	0.0333	0.7065	1.1563	1.0002
S K	2.71	1.69	0.0208	1.0288	0.7463	1.0006
ClK	1.19	0.67	0.0095	0.9804	0.8104	1.0002
SnL	0.85	0.14	0.0063	0.7857	0.9391	1.0000
PtL	31.02	3.17	0.2031	0.6464	1.0126	1.0000
Total	100.00	100.00				

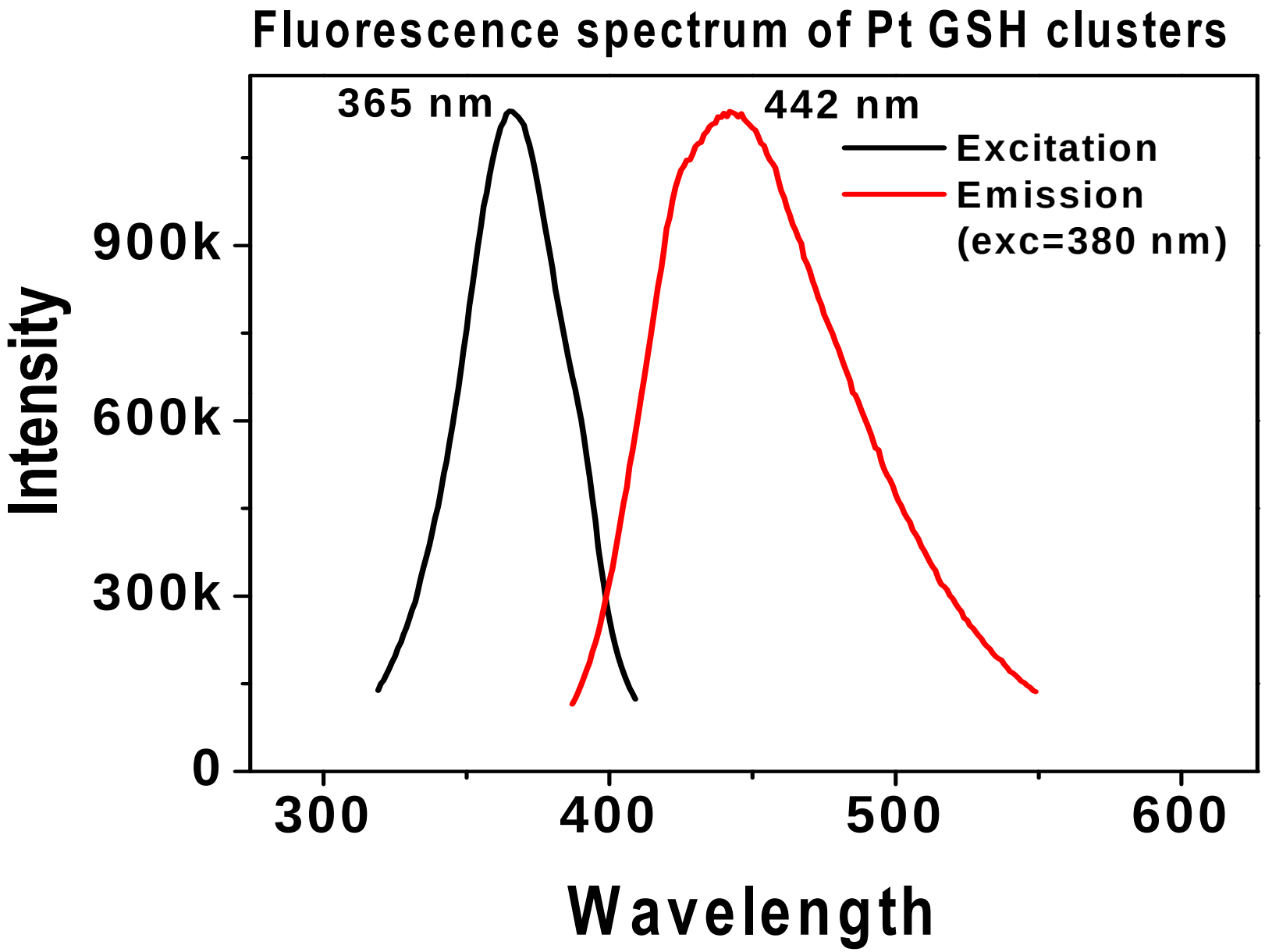


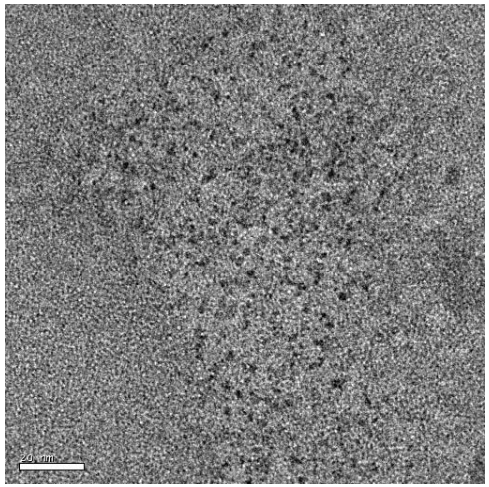

IR spectrum
Intensity(a.u)
OH str
3411
2401
2065
1637
C=O str
1382
1217
824
Pt@BSA clusters
BSA
GSH
4000
3000
2000
1000
0
Wavenumber(cm-1)

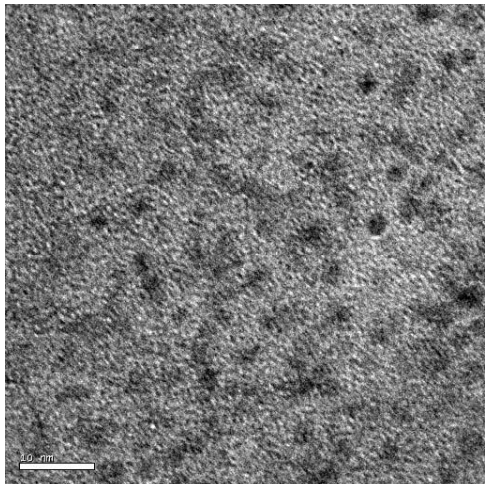

MALDI Data
4k
2k
0
Intensity
linear positive
6.8 kDa
13.6 kDa
31 kDa
10k
20k
30k
40k
m/z

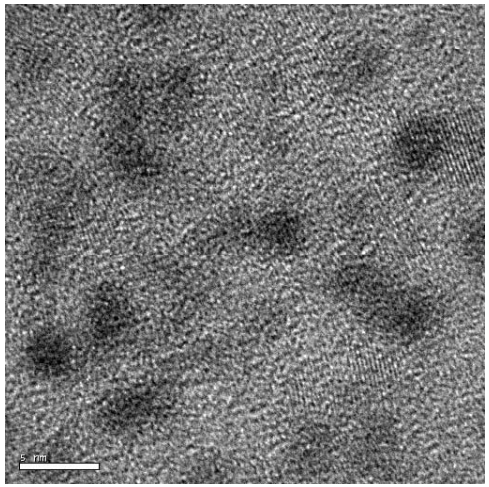
Synthesis of Pt@GSH clusters at room temperature by interfacial etching using Pt@GSH nanoparticles

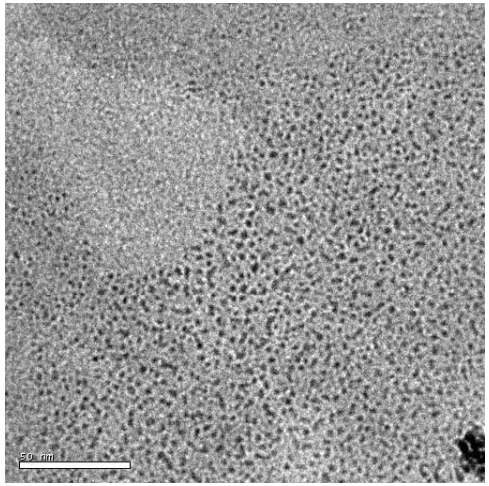

UV-VIS spectrum of Interfacial etching of Pt-GSH by excess GSH
Absorbance
1.0
0.5
0.0
200
400
600
800
1000
Wavelength(nm)
At '0' hour
After 2 hours
After 16 hours
after 18 hours
After 2 days

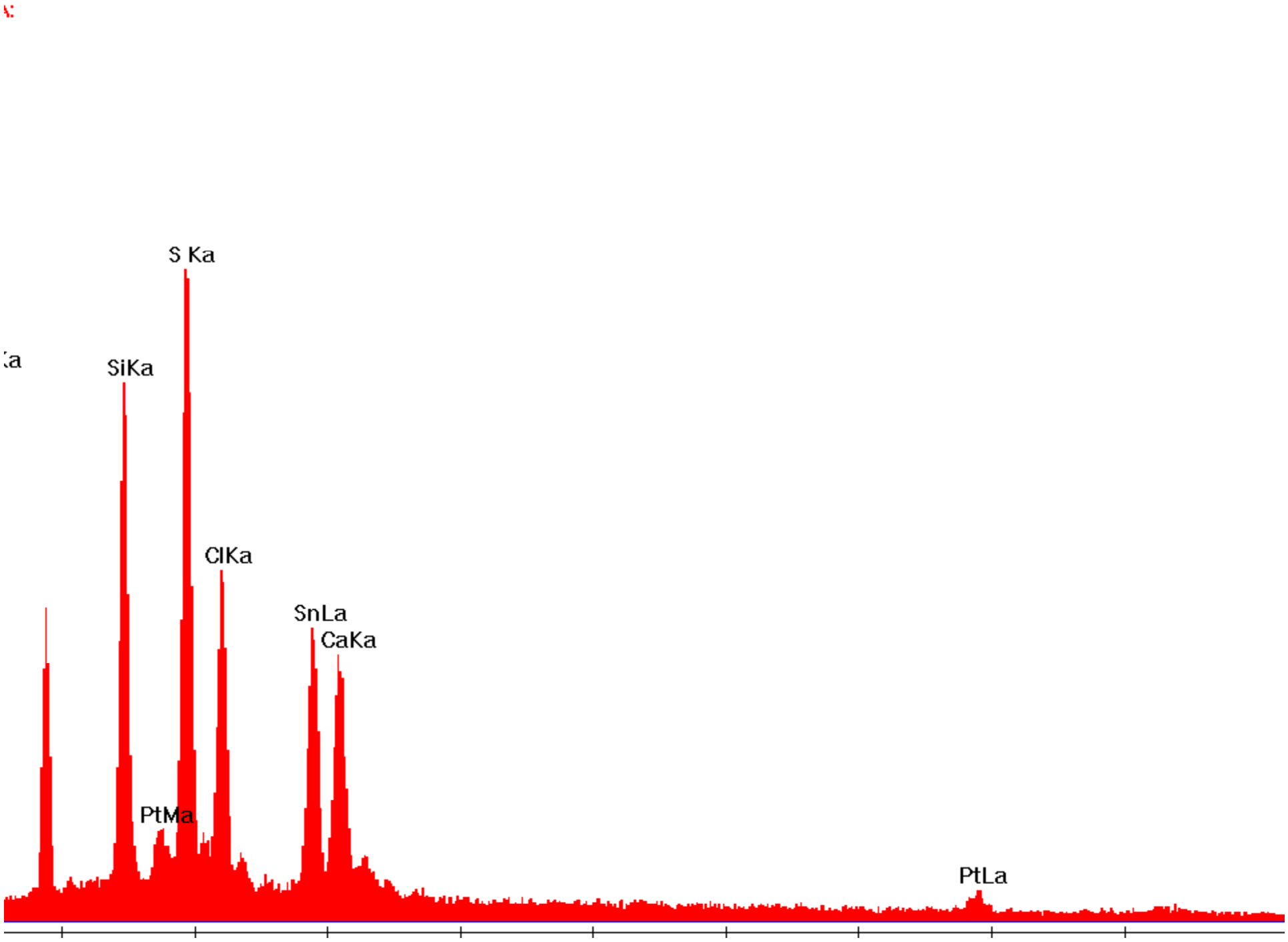

Fluorescence spectrum of Pt GSH clusters
365 nm
442 nm
Excitation
Emission
(exc=380 nm)
Intensity
900k
600k
300k
0
300
400
500
600
Wavelength


20 nm

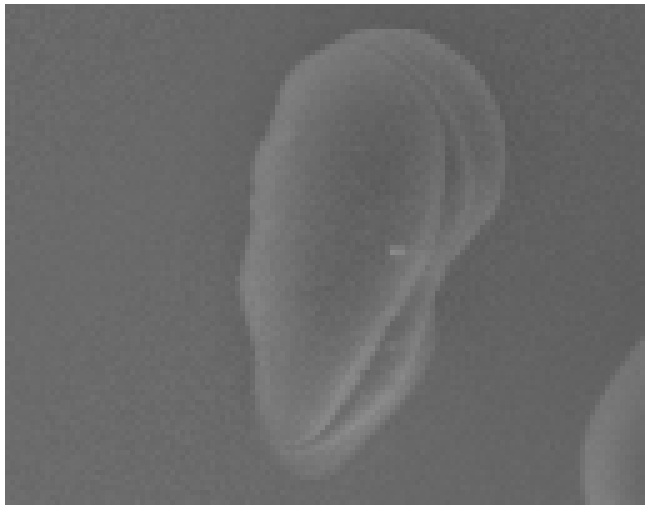

10 nm

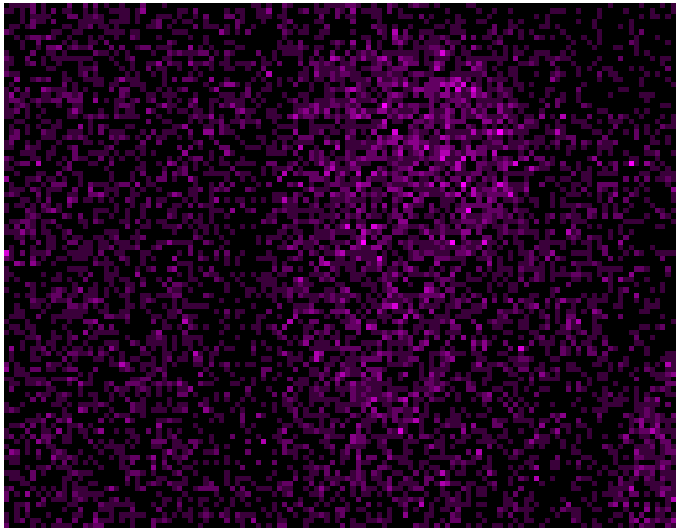

5 nm

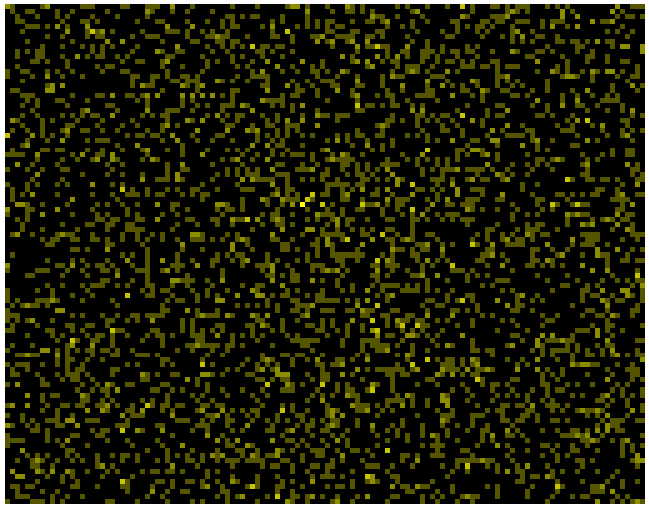

50 nm

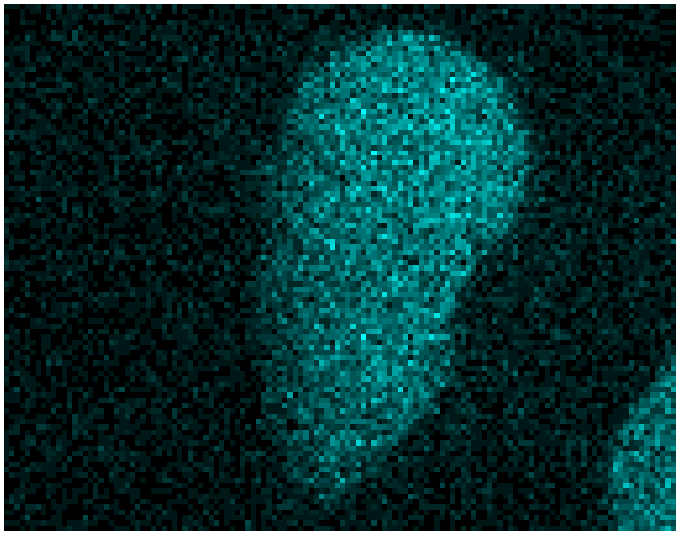

S Ka
SiKa
ClKa
SnLa
CaKa
PtMa
PtLa

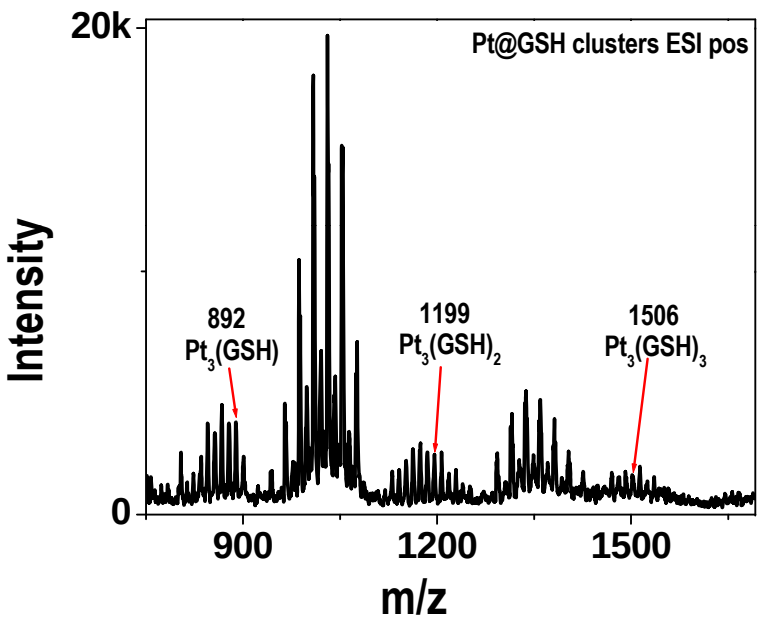
Images

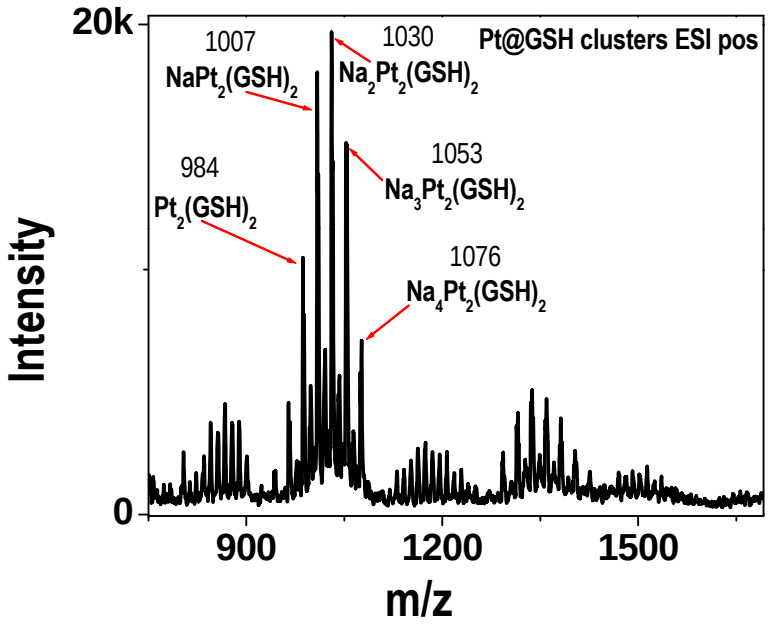









20k
0
Intensity
Pt@GSH clusters ESI pos
892
Pt3(GSH)
1199
Pt3(GSH)2
1506
Pt3(GSH)3
900
1200
1500
m/z


20k
0
Intensity
Pt@GSH clusters ESI pos
1007
NaPt2(GSH)2
1030
Na2Pt2(GSH)2
984
Pt2(GSH)2
1053
Na3Pt2(GSH)2
1076
Na4Pt2(GSH)2
900
1200
1500
m/z


Tag By Adam
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