Advanced Nanosensors for Continuous Monitoring of Heavy Metals

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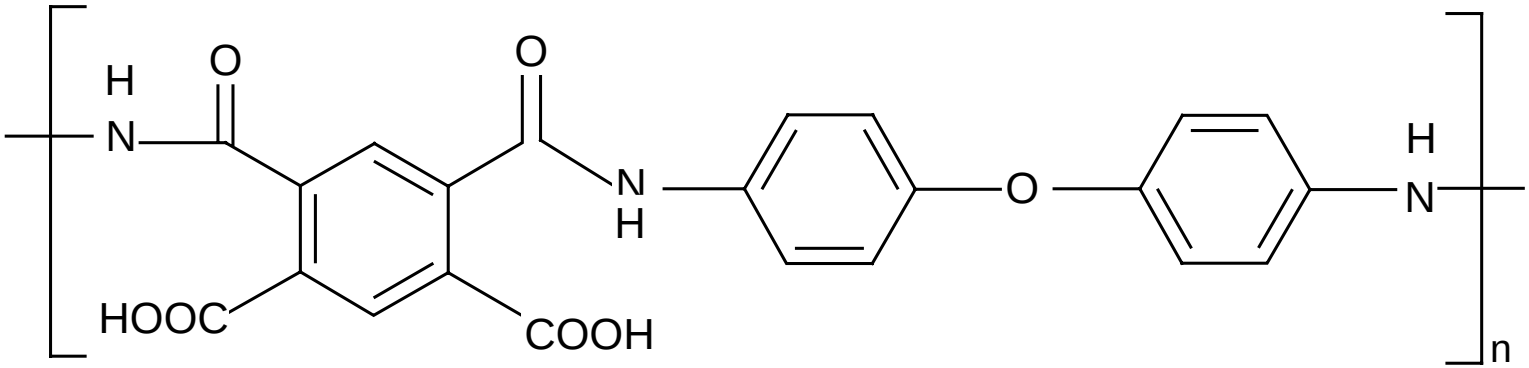
Philadelphia, PA.

Metal Polymer Nanocomposites

- Applications
  - Sensors
  - Catalysis
  - Nanoelectronics
    - Magnetic recording and information storage
    - MRI enhancement and medical diagnostics

Polyamic Acid

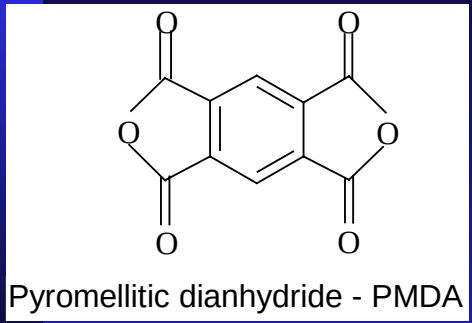


Objectives

- To synthesize Au nanoparticles in organic medium using a short, simple and convenient method.

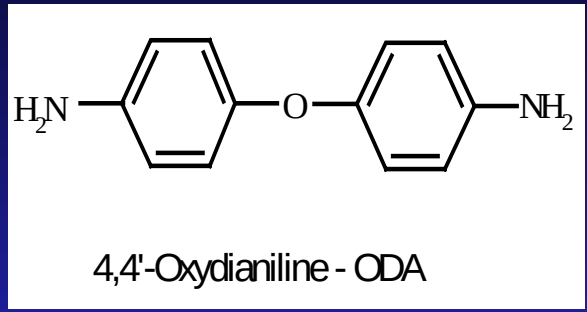
- To study the potential of the PAA-metal nanoparticle films for the analysis and removal of heavy metals from aqueous medium

PAA Synthesis and Chemistry



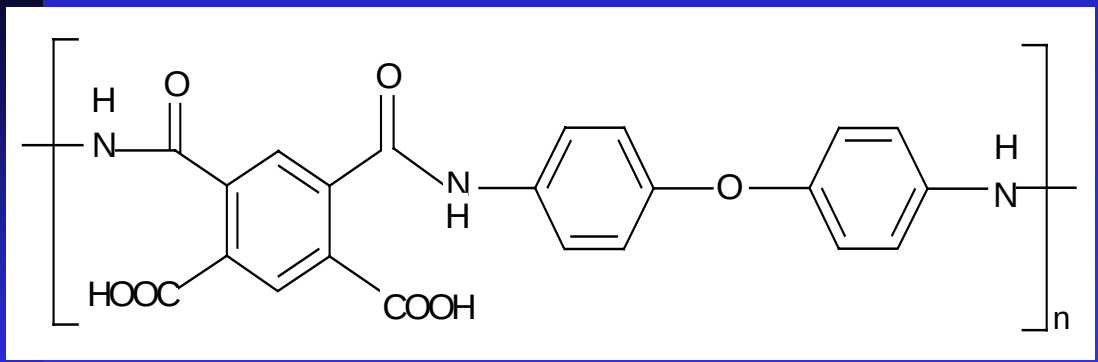
Pyromellitic dianhydride - PMDA

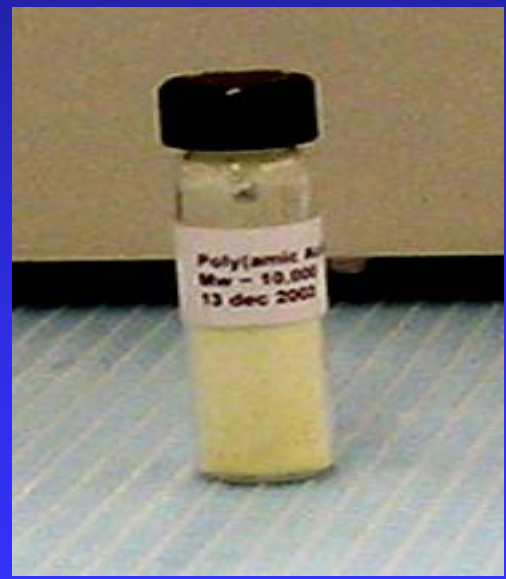
+



4,4'-Oxydianiline - ODA

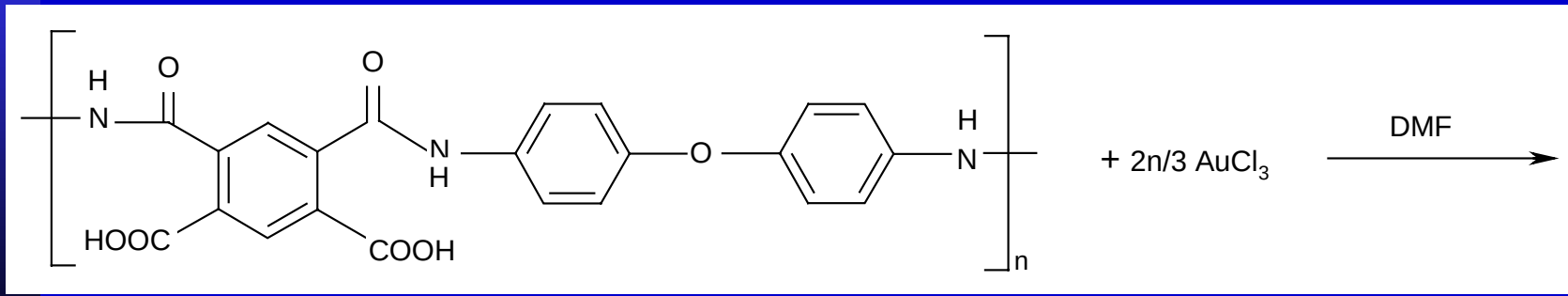
MeCN, rt
Stir, 1 hr, filter

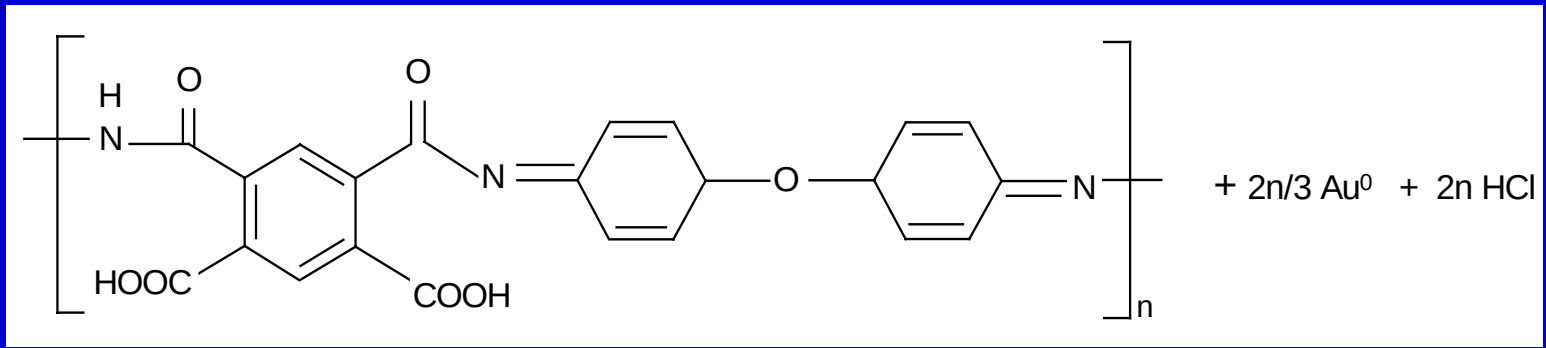




Mw = 10,000 (by GPC)

One Pot Synthesis of Stable NPs



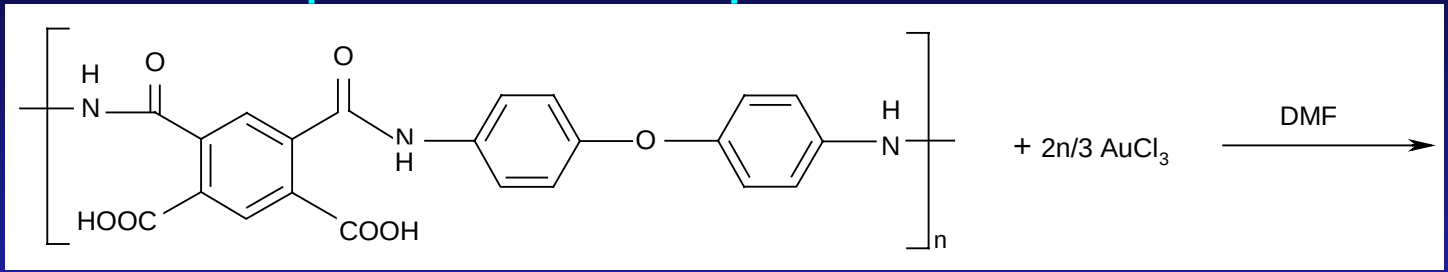


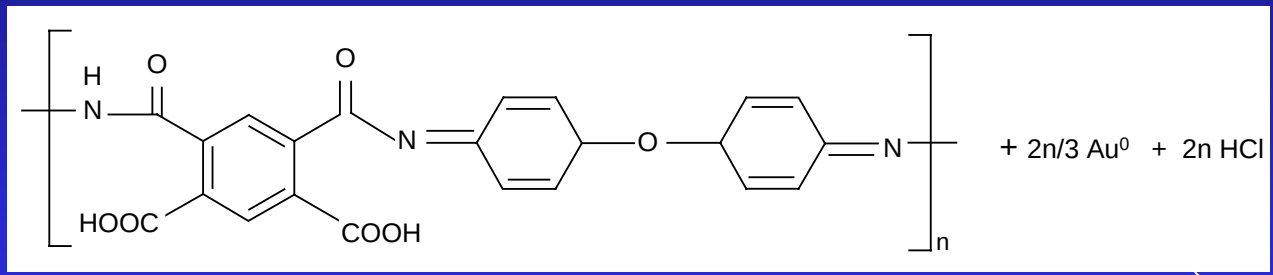
PAA-capped Gold nanoparticles-Single phase, stable and monodispersed

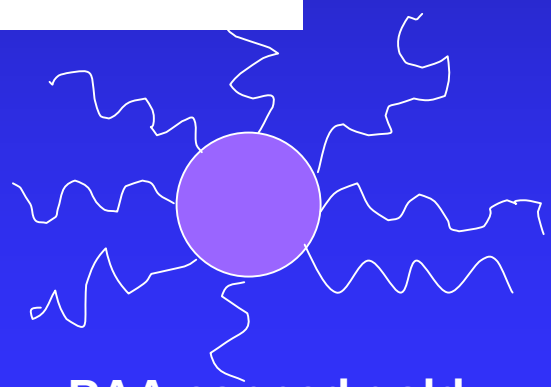
Adam K. Wanekaya, Daniel Andreescu, J. Wang,
Omowunmi A. Sadik, Journal of American Chemical Society, 2004 (In Press)

Synthesis

PAA was dissolved in DMF and solid $AuCl_3$ was added to it. The reaction was allowed to proceed at room temperature





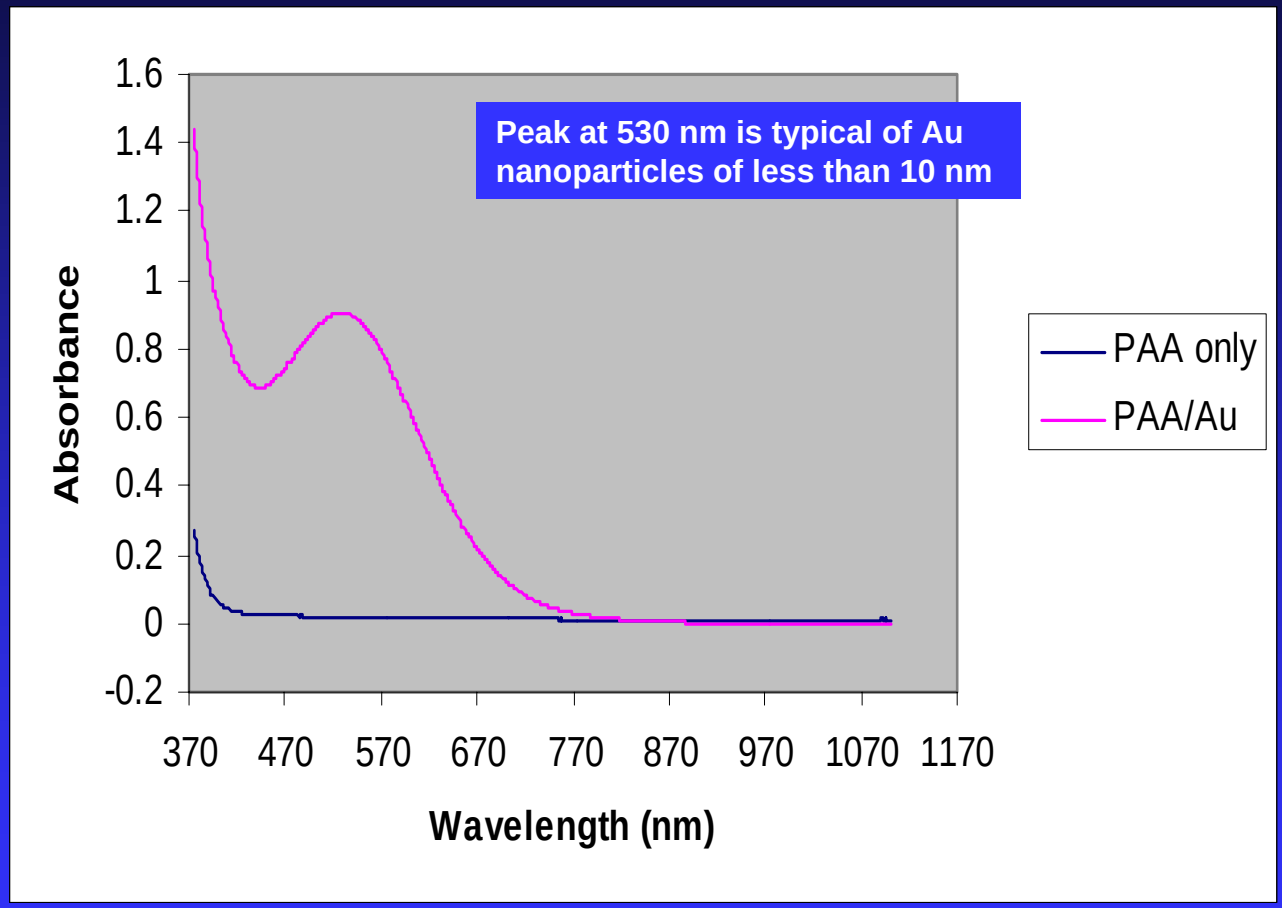


PAA capped gold nanoparticles

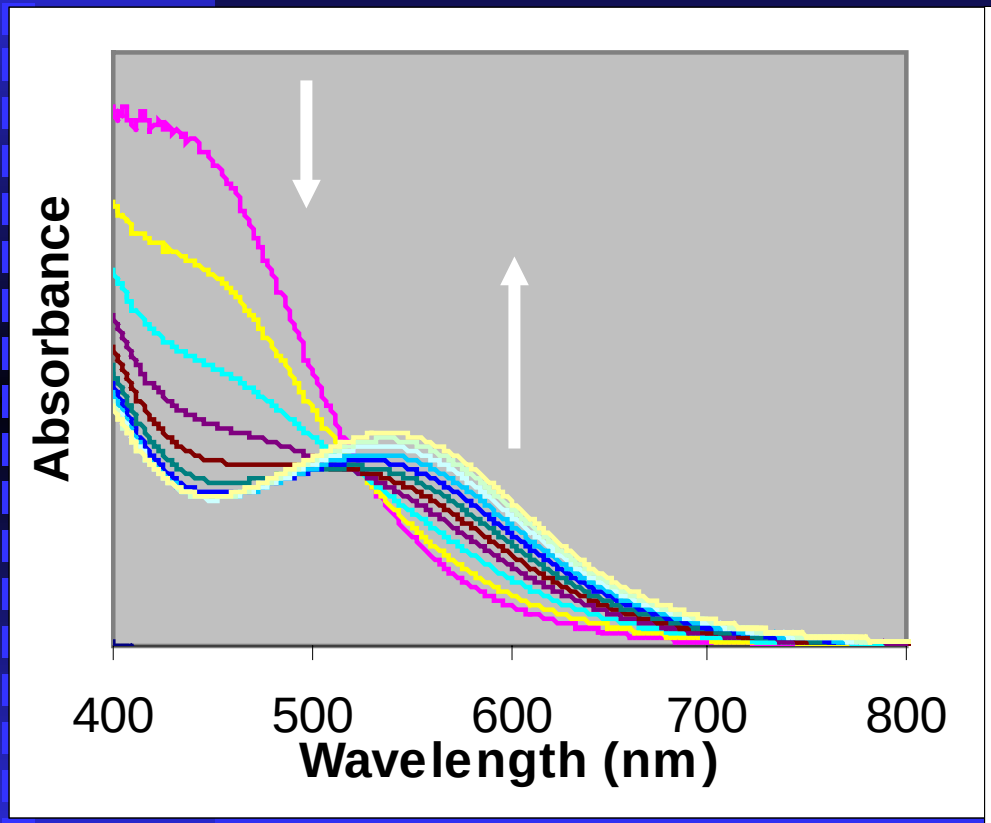
Characterization

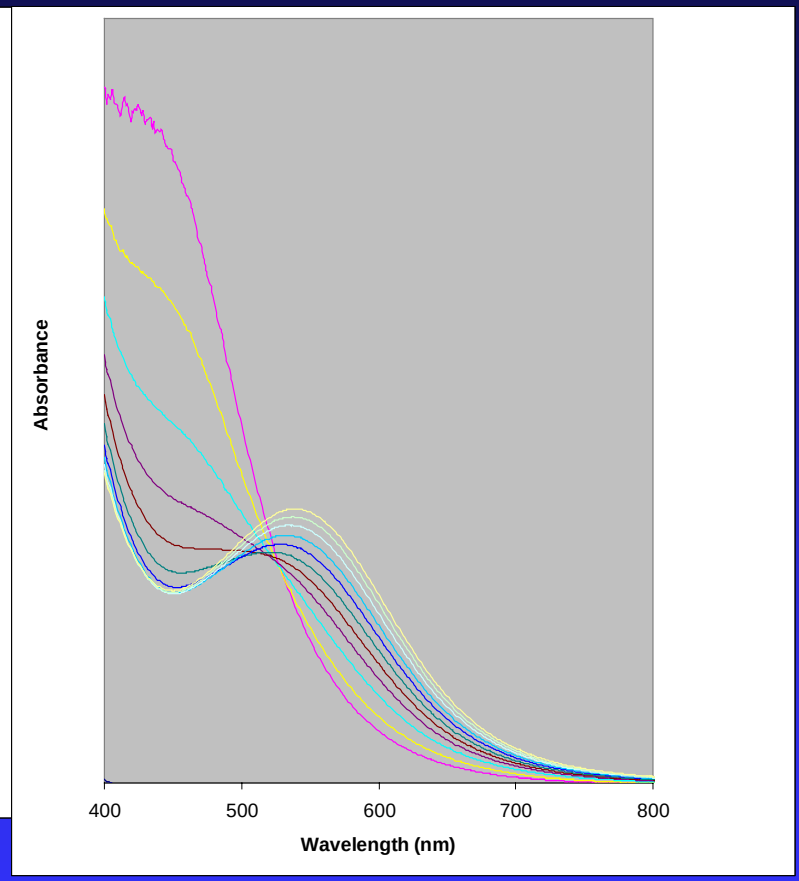
- UV/Visible Spectroscopy
- SEM
- TEM
- Electrochemical(conductivity, electroactivity)
- EDS(elemental composition)

Absorption Spectrum



Time-dependent Absorbance Spectra

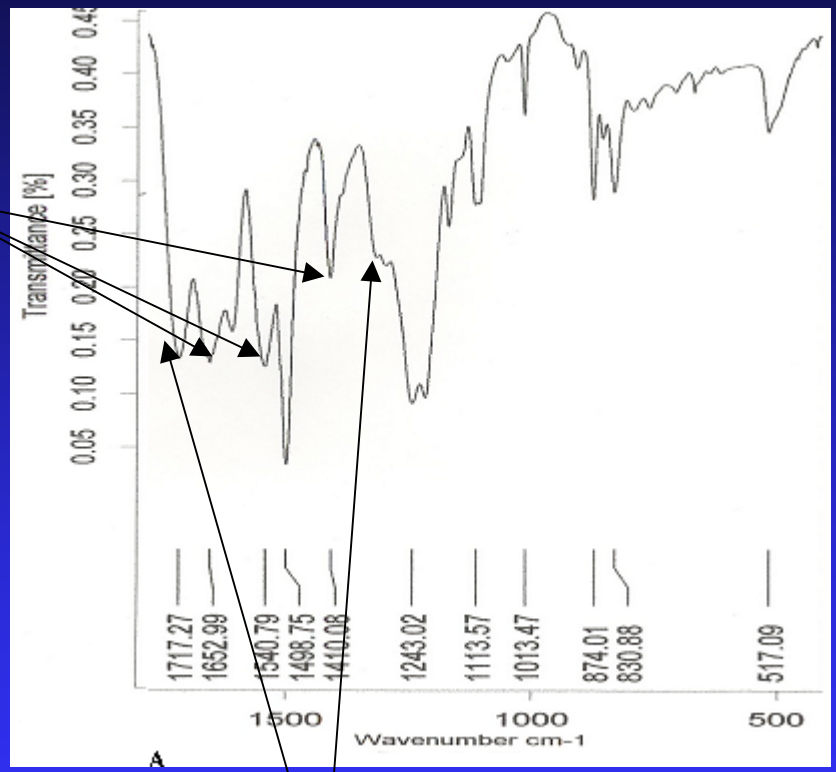




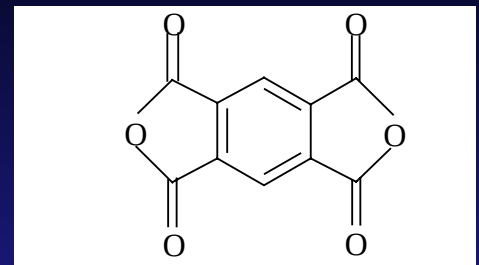
Time dependent UV-VIS spectrum after the addition of 1.5 mg $AuCl_3$ to a 4 mL dimethylformamide solution containing 1 mg of PAA to form PAA-capped gold nanoparticles: a) 1 min b) 5 min c) 10 min d) 15 min e) 20 min f) 25 min g) 30 min h) 35 min i) 40 min j) 45 min k) 50 min.

PAA Characterization Infrared

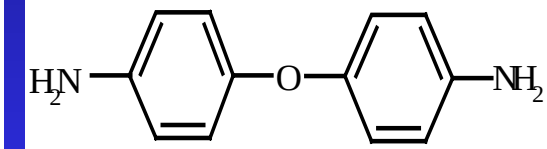
Amide Vibes



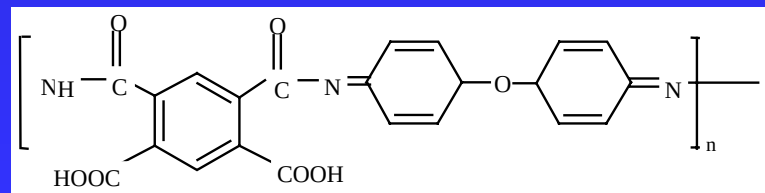
COOH Vibes



Pyromellitic dianhydride - PMDA

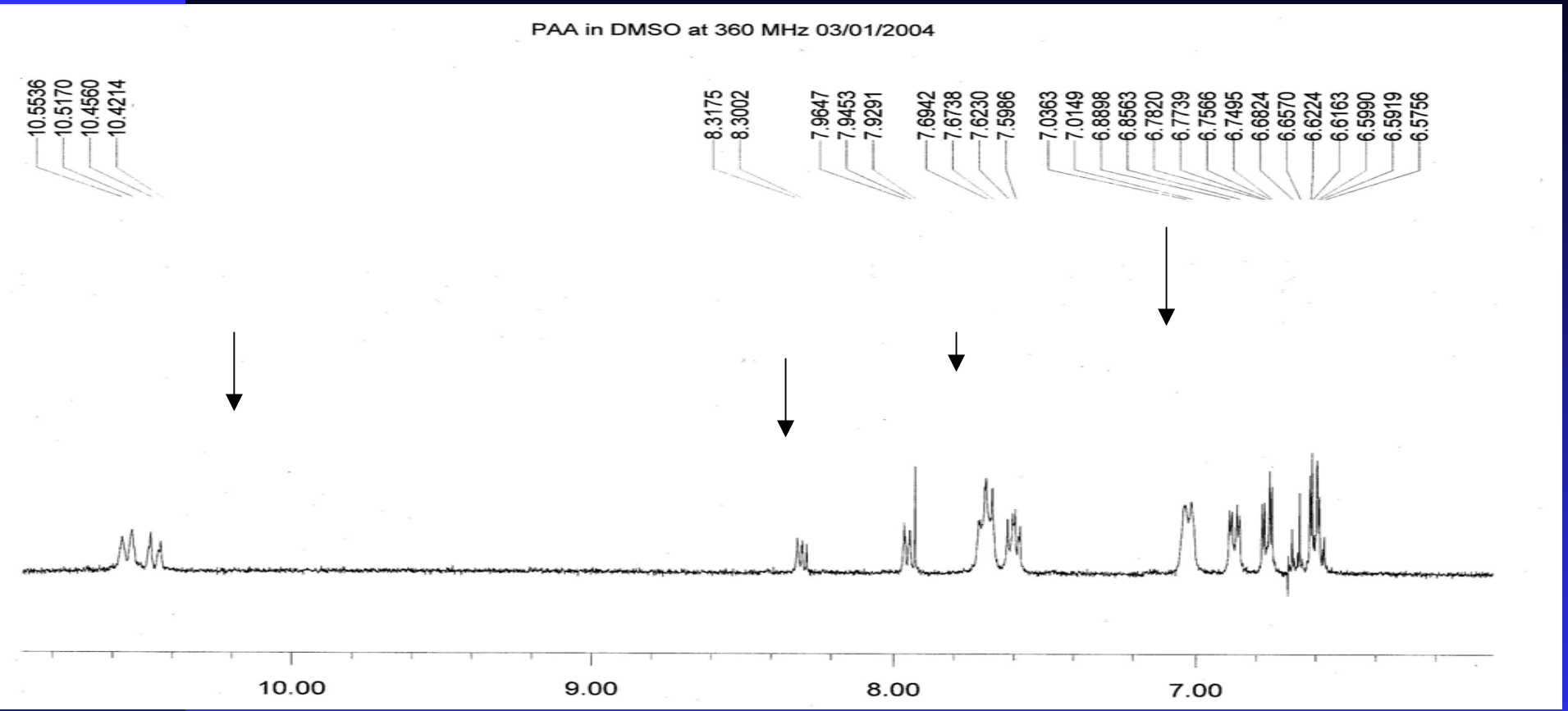


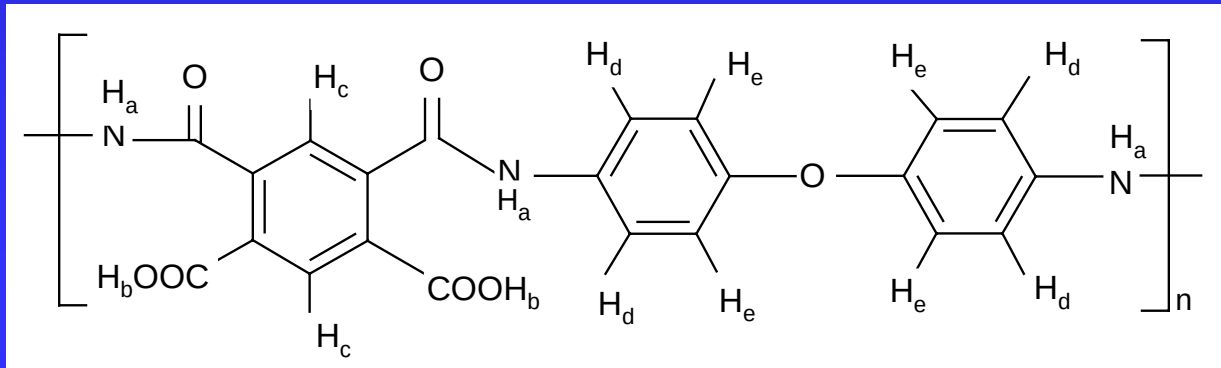
4,4'-Oxydianiline - ODA



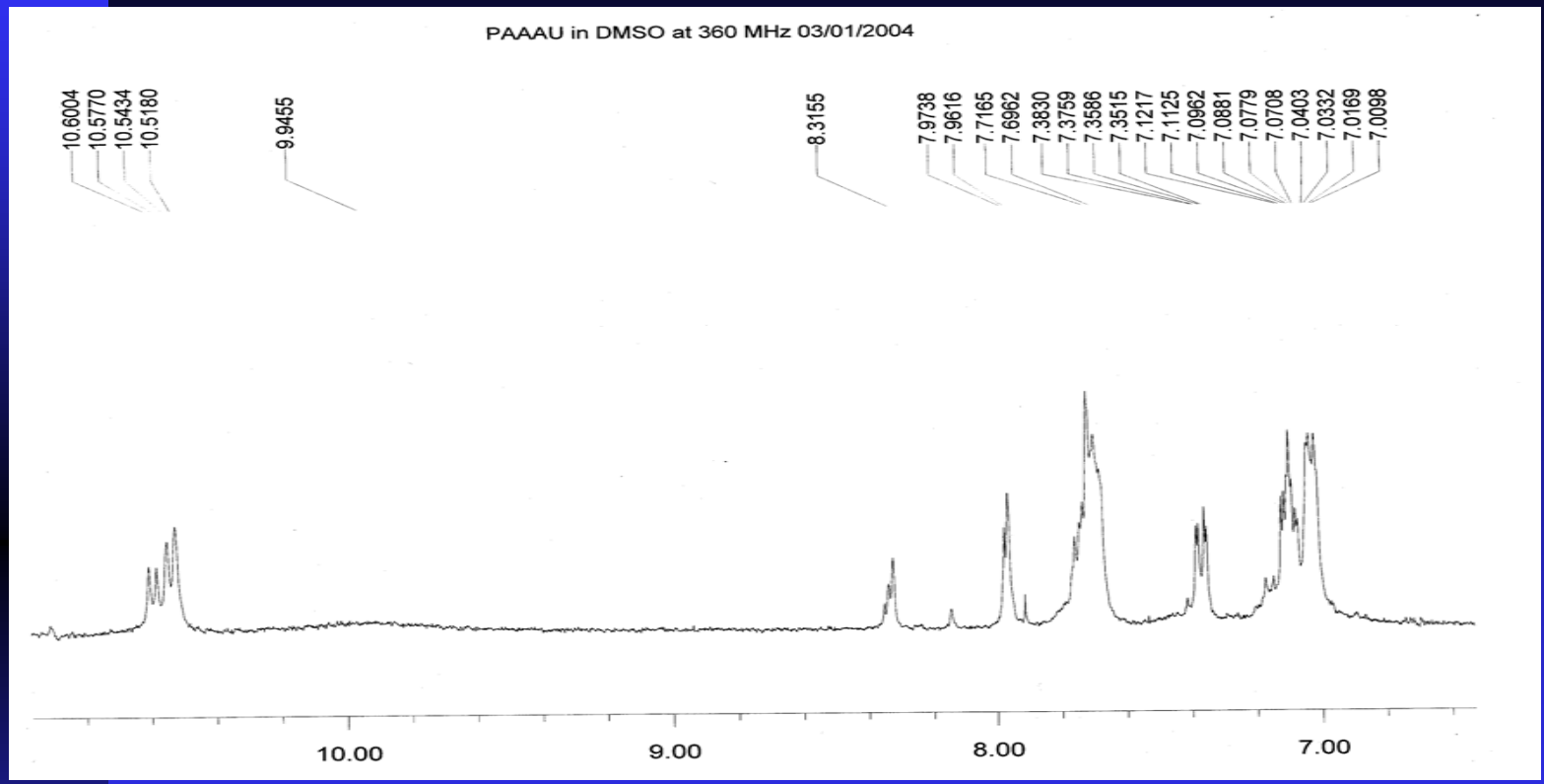
Poly(amic acid)- PAA

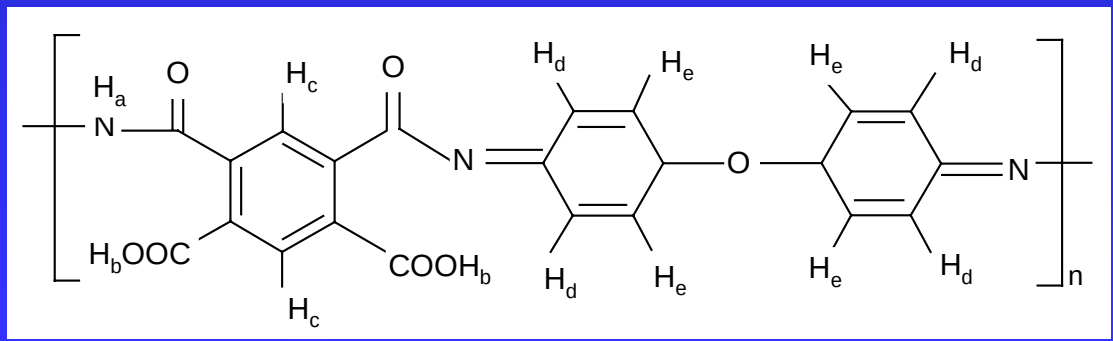
^{1}HNMR of PAA


PAA in DMSO at 360 MHz 03/01/2004
10.5536
10.5170
10.4560
10.4214
8.3175
8.3002
7.9647
7.9453
7.9291
7.6942
7.6738
7.6230
7.5986
7.0363
7.0149
6.8898
6.8563
6.7820
6.7739
6.7566
6.7495
6.6824
6.6570
6.6224
6.6163
6.5990
6.5919
6.5756
10.00
9.00
8.00
7.00

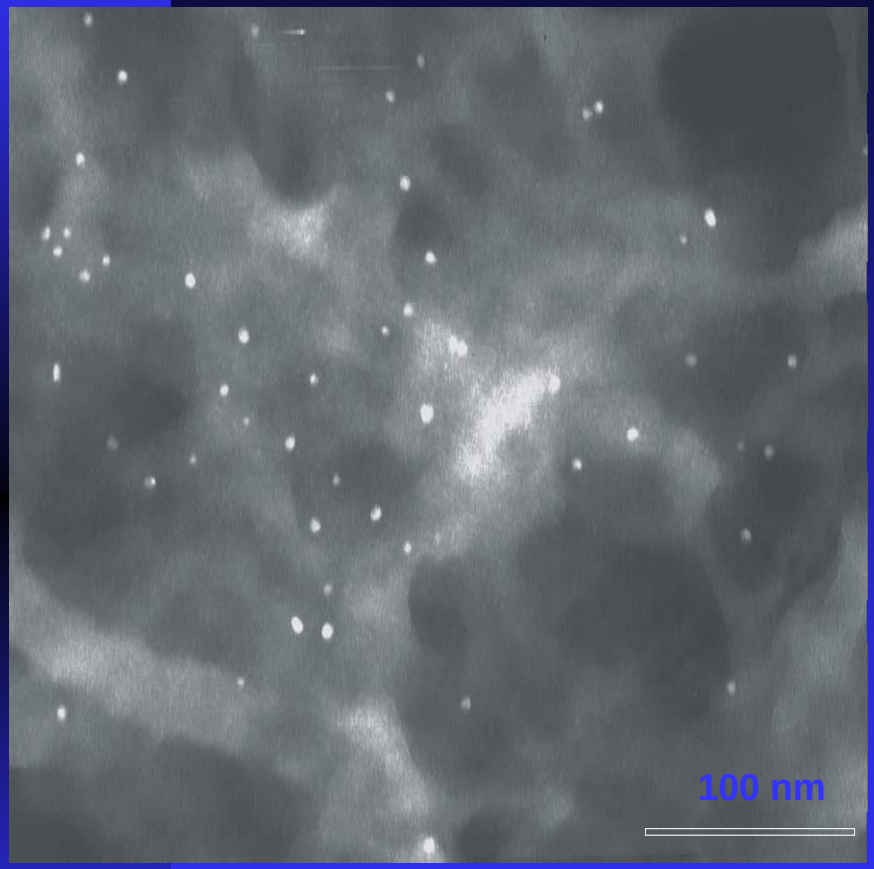

Ha
N
O
Hc
O
N
Ha
HbOOC
COOHb
Hc
Hd
He
O
He
Hd
Ha
N
Hd
He
He
Hd
n

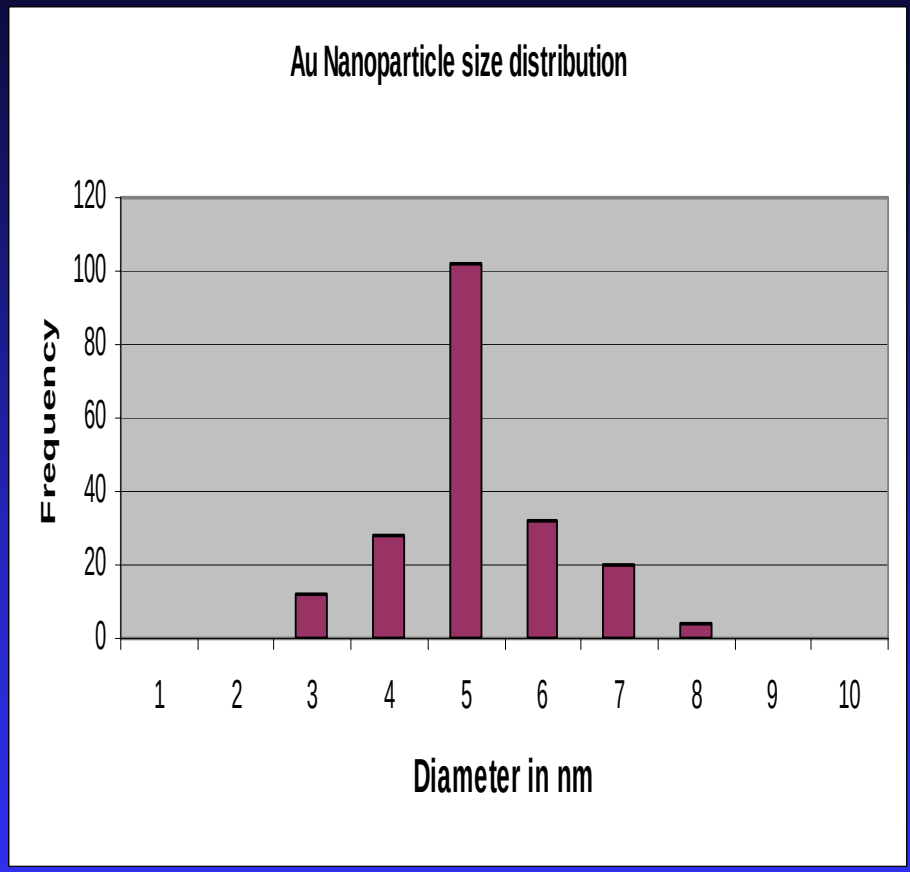
NMR of PAA oxidized by Au Nanoparticles





Particle Size and Distribution

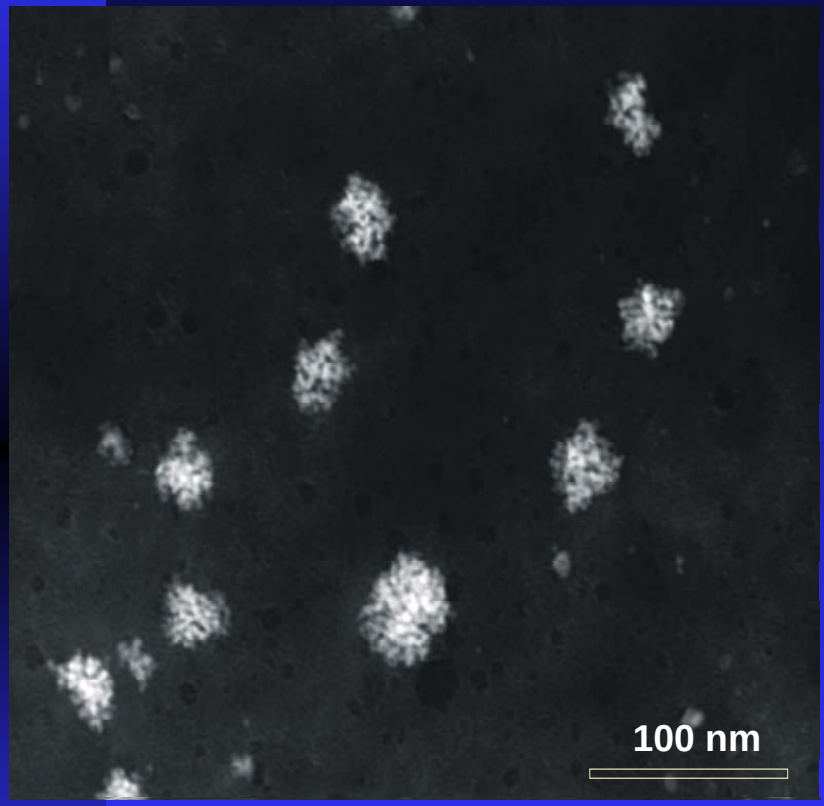




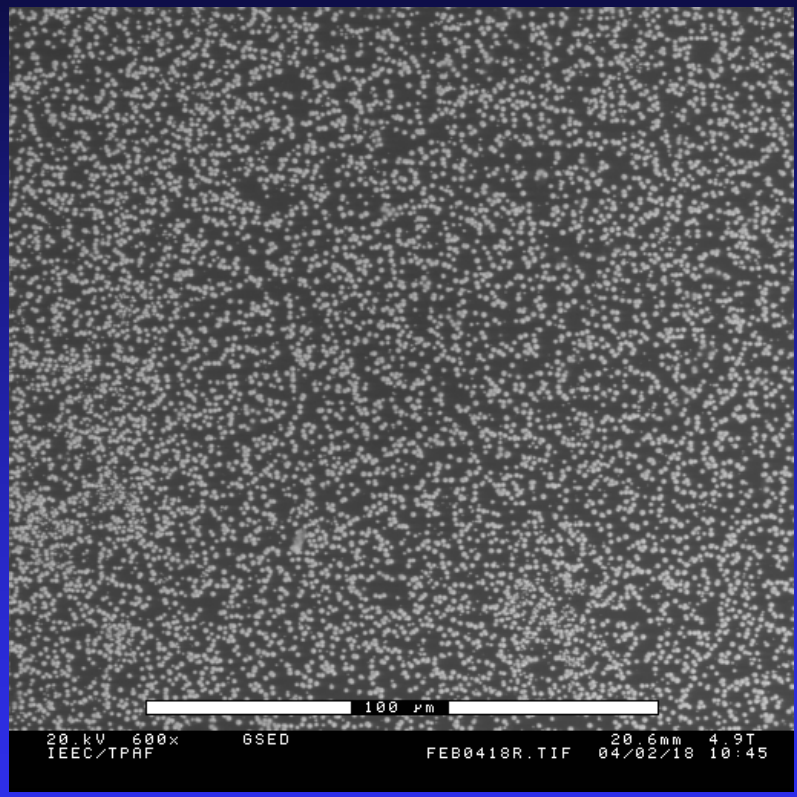
TEM of the well dispersed Au nanoparticles from reduction of 1.5 mg $AuCl_3$ by 6mL of 0.16 mg/mL PAA in DMF

Average particle size: 5.11 ± 0.89 nm (from 200 particles)

TEM and SEM Images

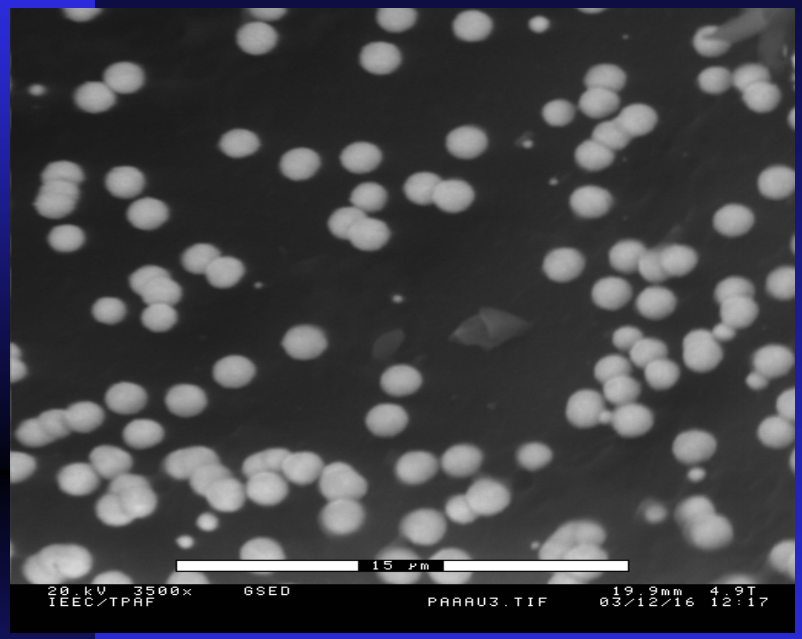


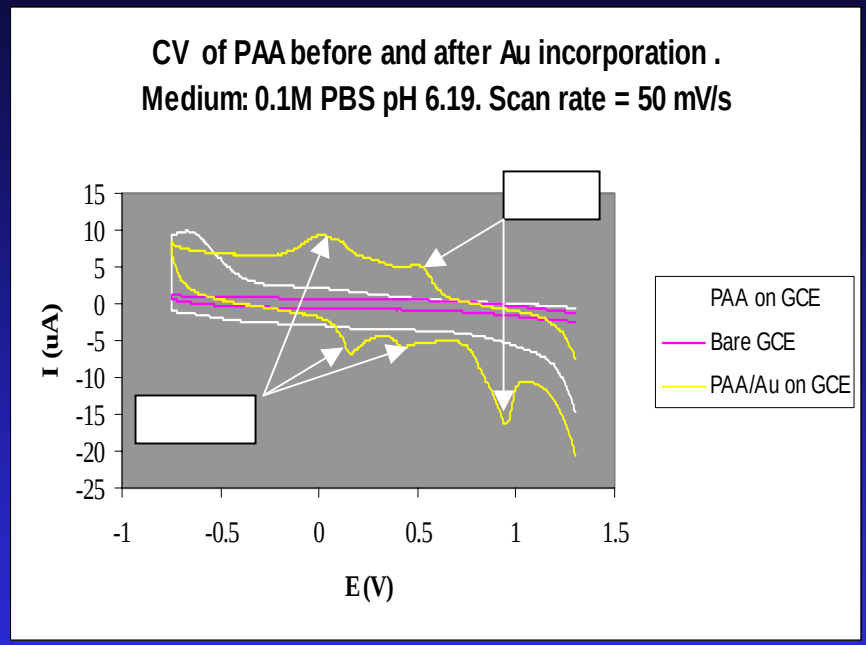
TEM of the Au nanoparticles agglomerates from reduction of 10 mg $AuCl_3$ by 2mL of 10 mg/mL PAA in DMF and diluted to 100 mL

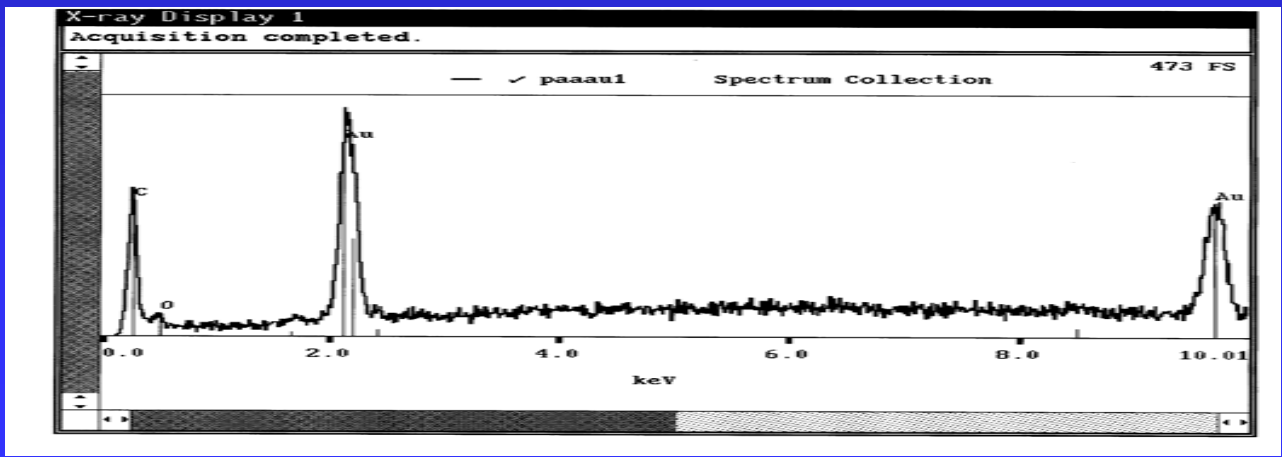


SEM Images of Au Nanoparticle agglomerates on PAA film deposited on GCE x 600

SEM and Elemental Analysis

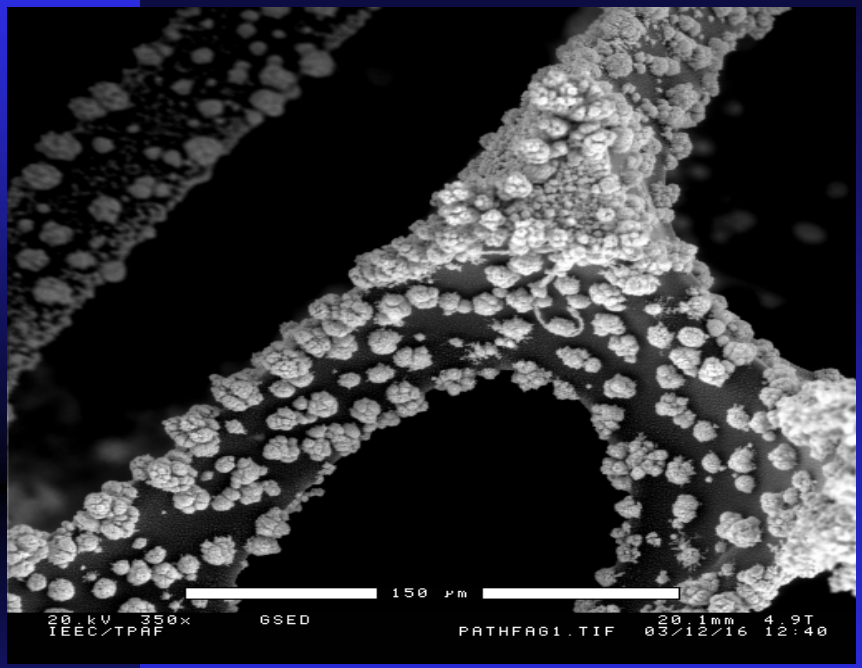


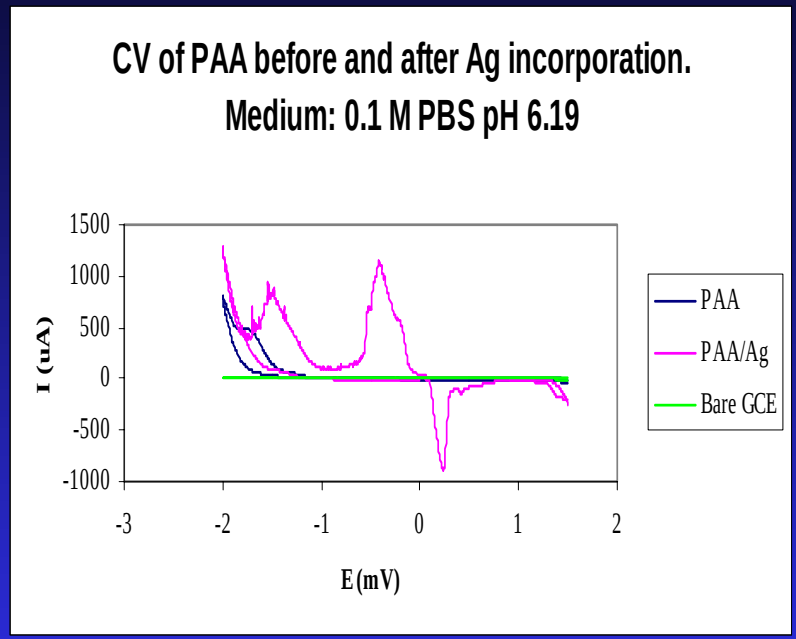


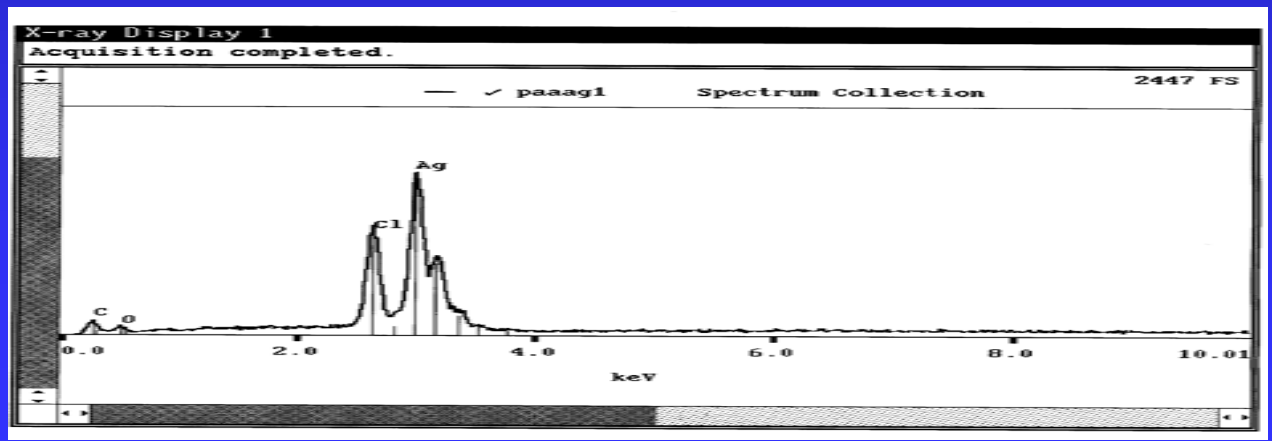


Energy dispersive spectrum of the Au Nanoparticles on PAA film deposited on GCE

Ag Nanoparticles

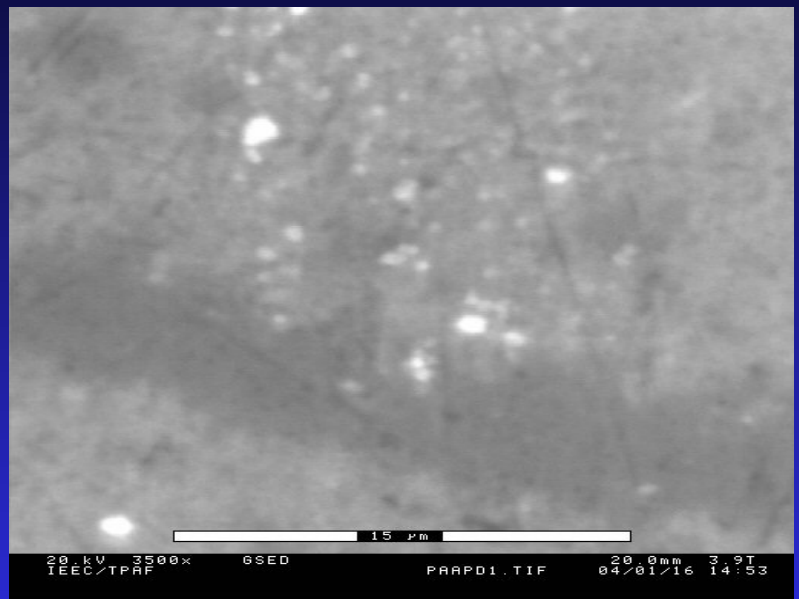


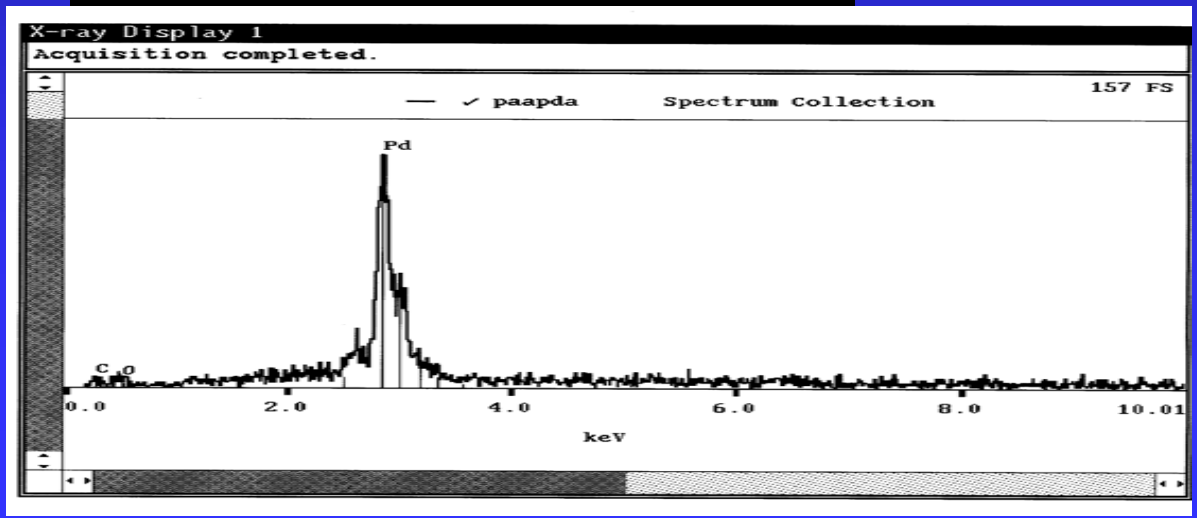




Energy dispersive spectrum of the Ag Nanoparticles on PAA film deposited on RVC

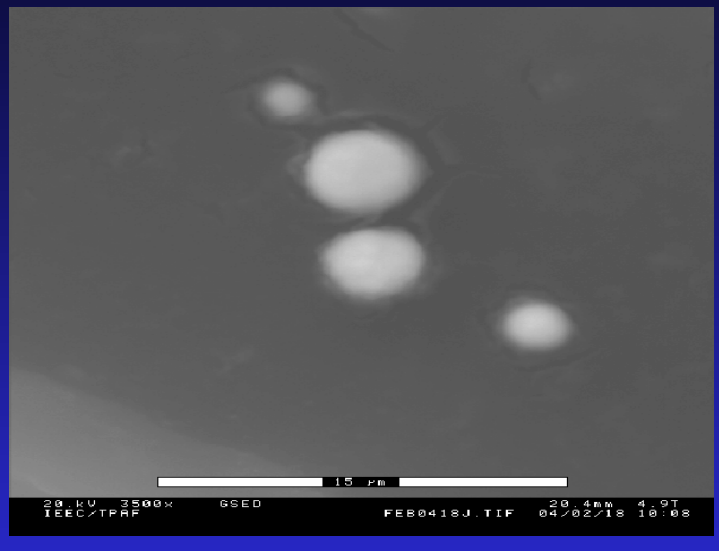
Pd Nanoparticles

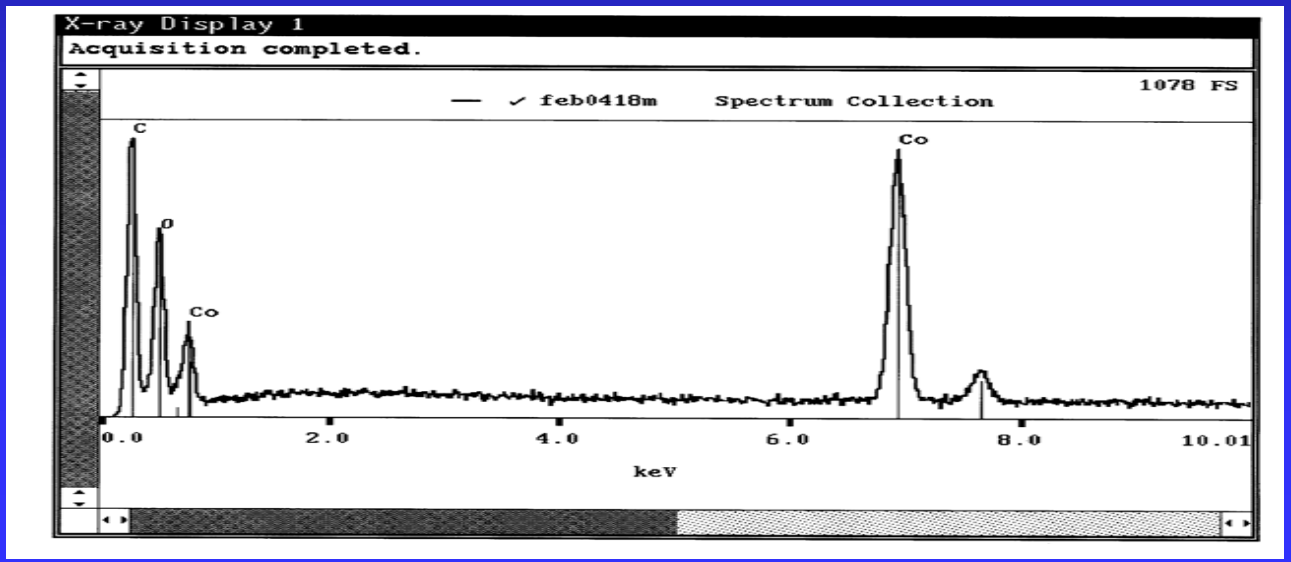




Energy dispersive spectrum of the Au Nanoparticles on PAA film deposited on GCE

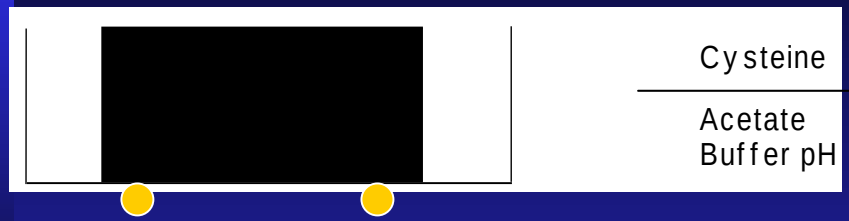
Co Nanoparticles

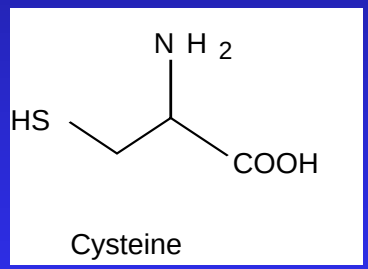


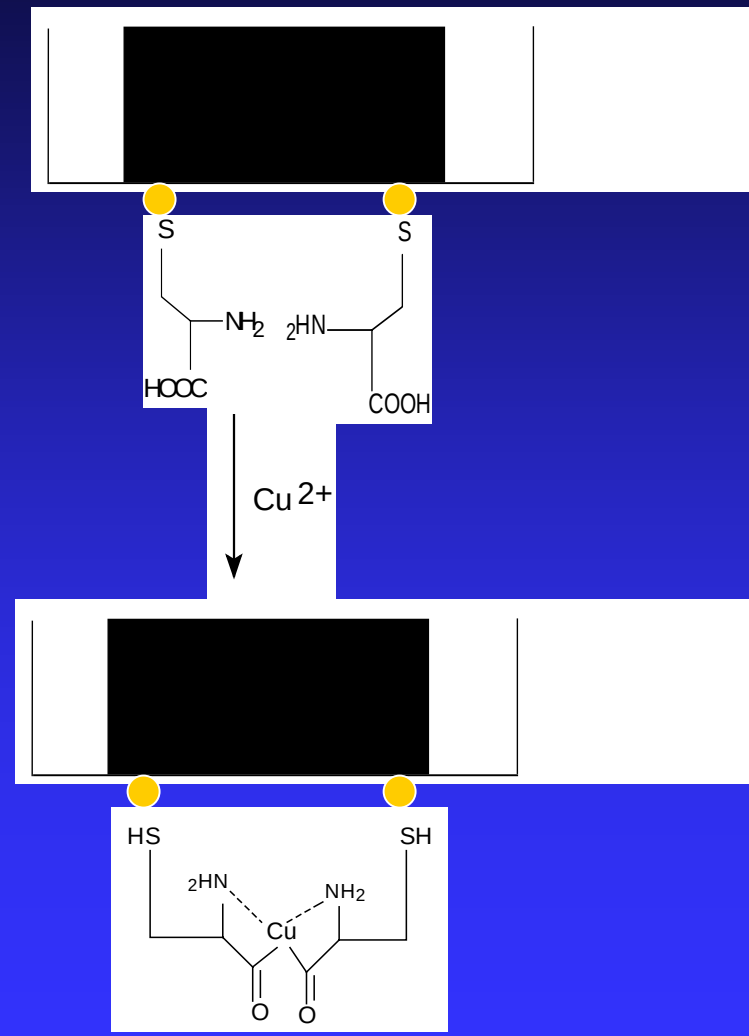


Energy dispersive spectrum of the Ag Nanoparticles on PAA film deposited on RVC

Preliminary Environmental Application

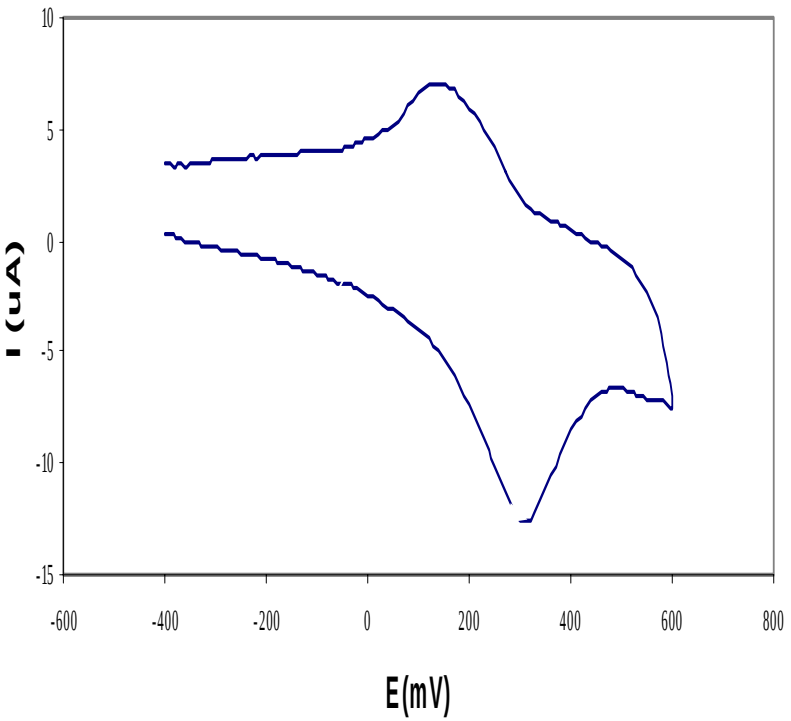




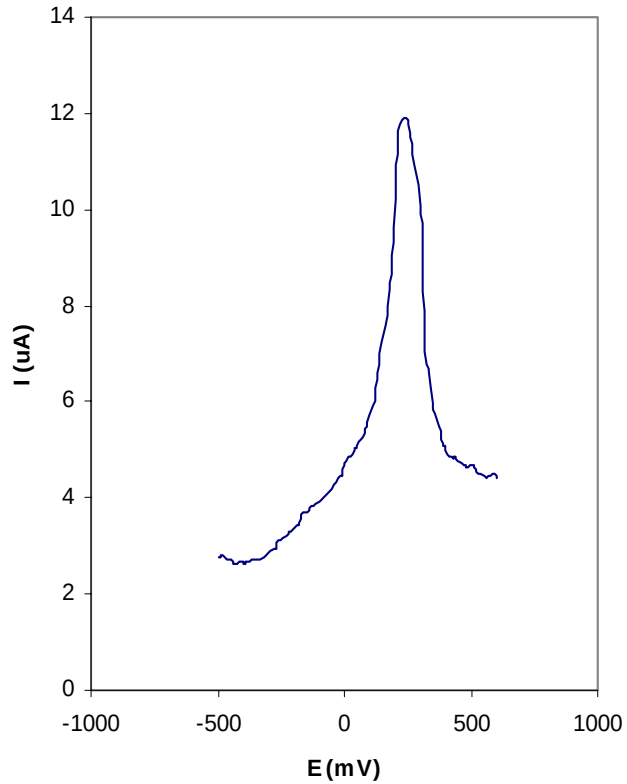


Metal Sensing

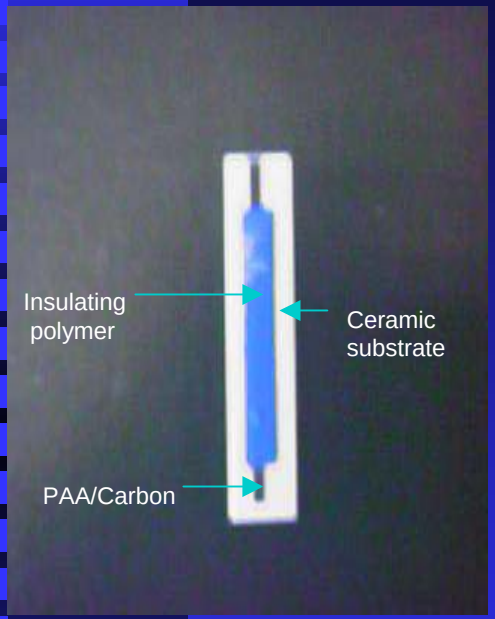
CV of PAA-Au-Cyst-Cu in Acet Buffer pH 4. Accumulation time = 20 min in 1ppm Cu in buffer. Scan Rate = 50 mV/s



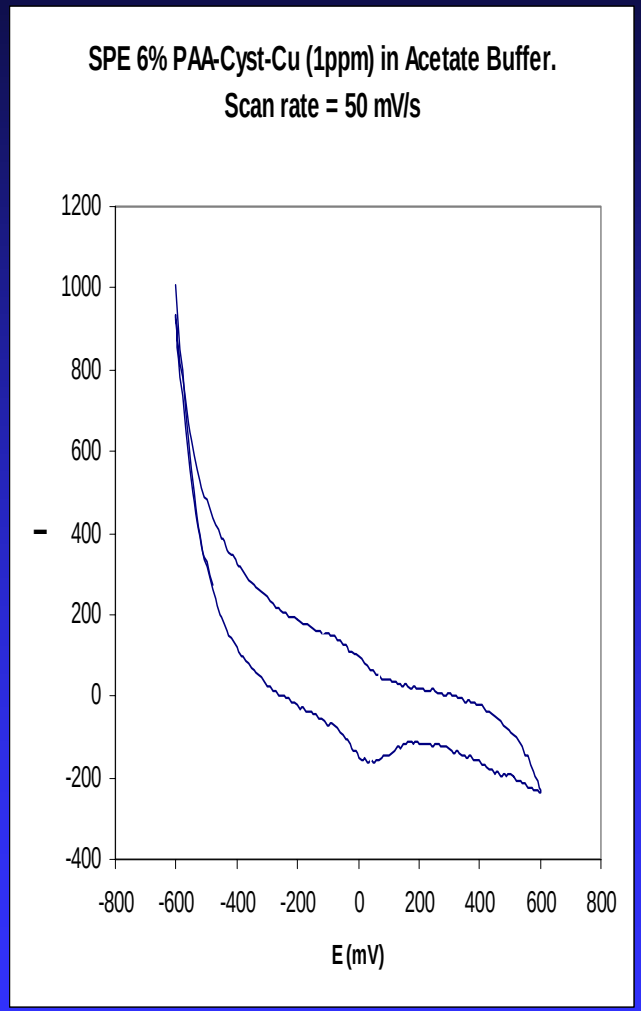
DPASV of PAA-AuNP-Cys-Cu in acetate buffer pH 4. Accumulation time = 20 min in acetate buffer. Voltammetric conditions: reduction potential= -1 V, scan rate = 50 mV/s

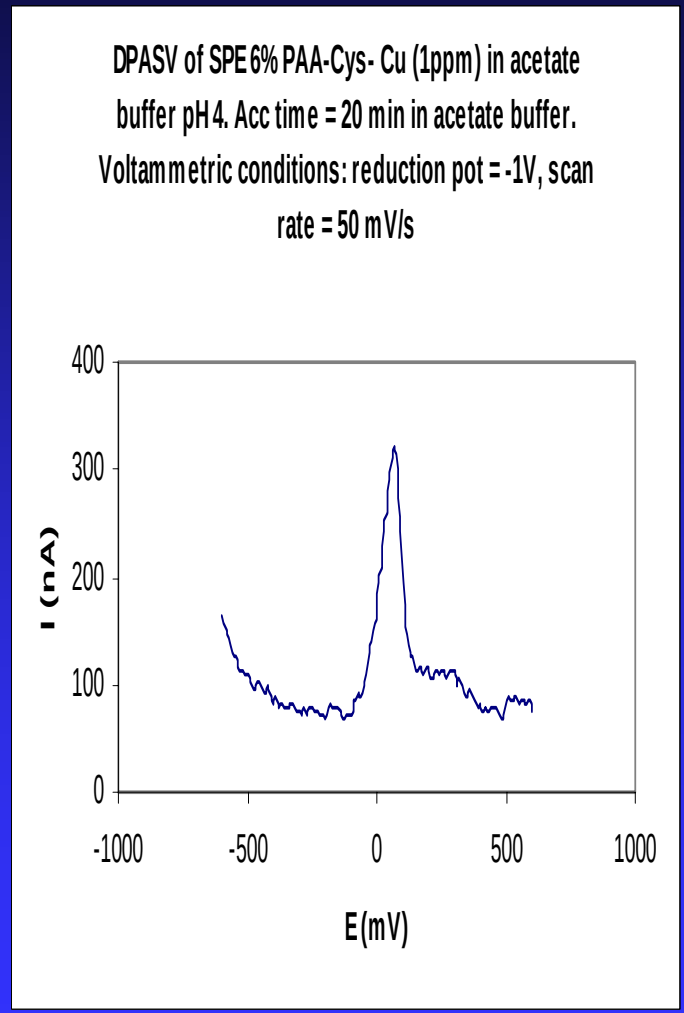


Screen-Printed Electrodes

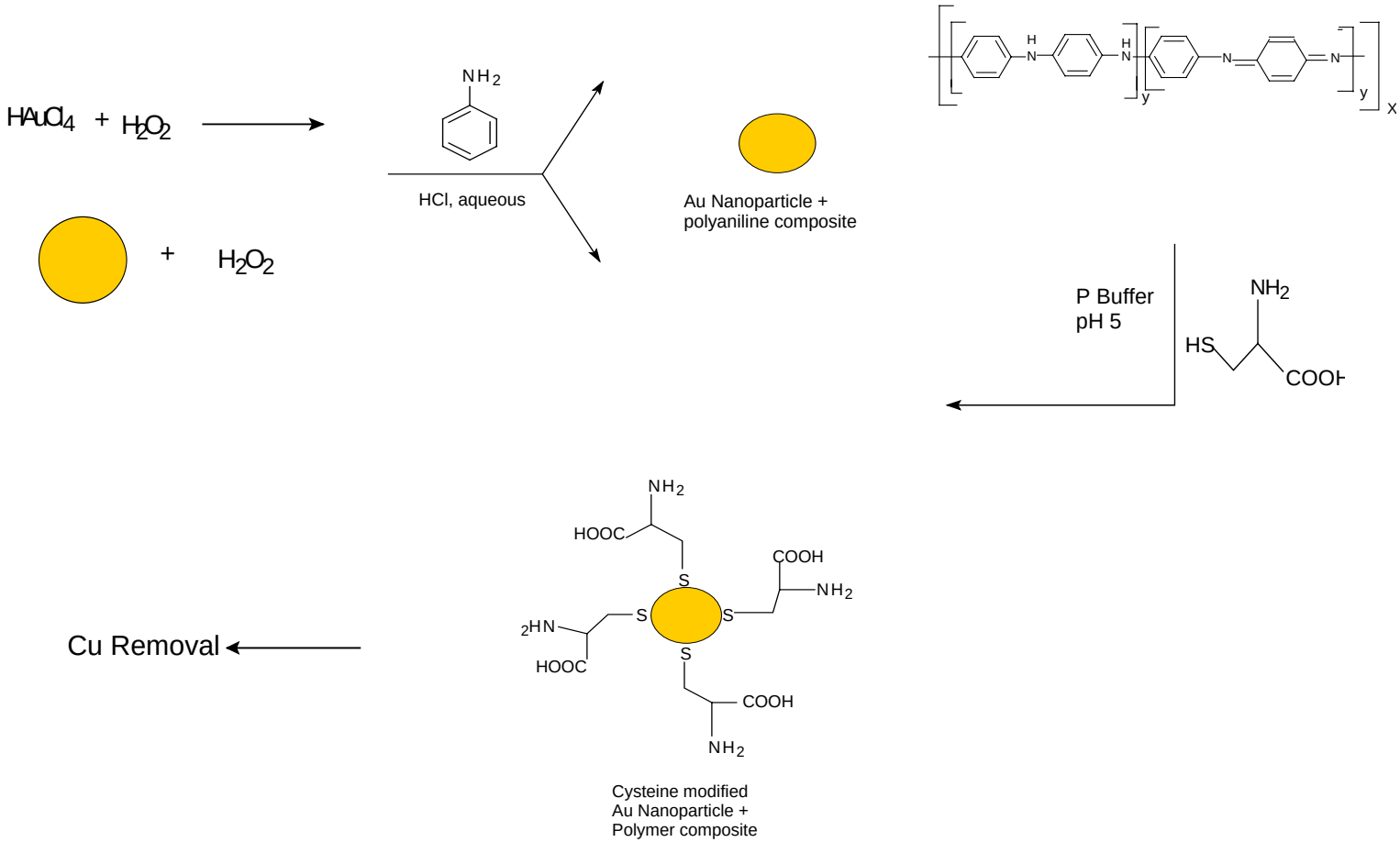


PAA Modified Screen Printed Electrode





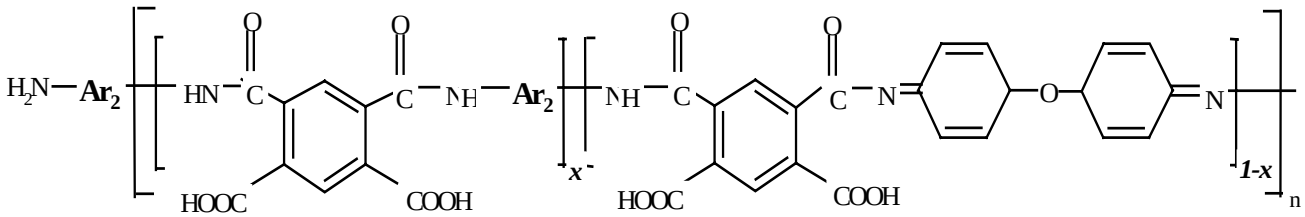
Selective Removal of Copper

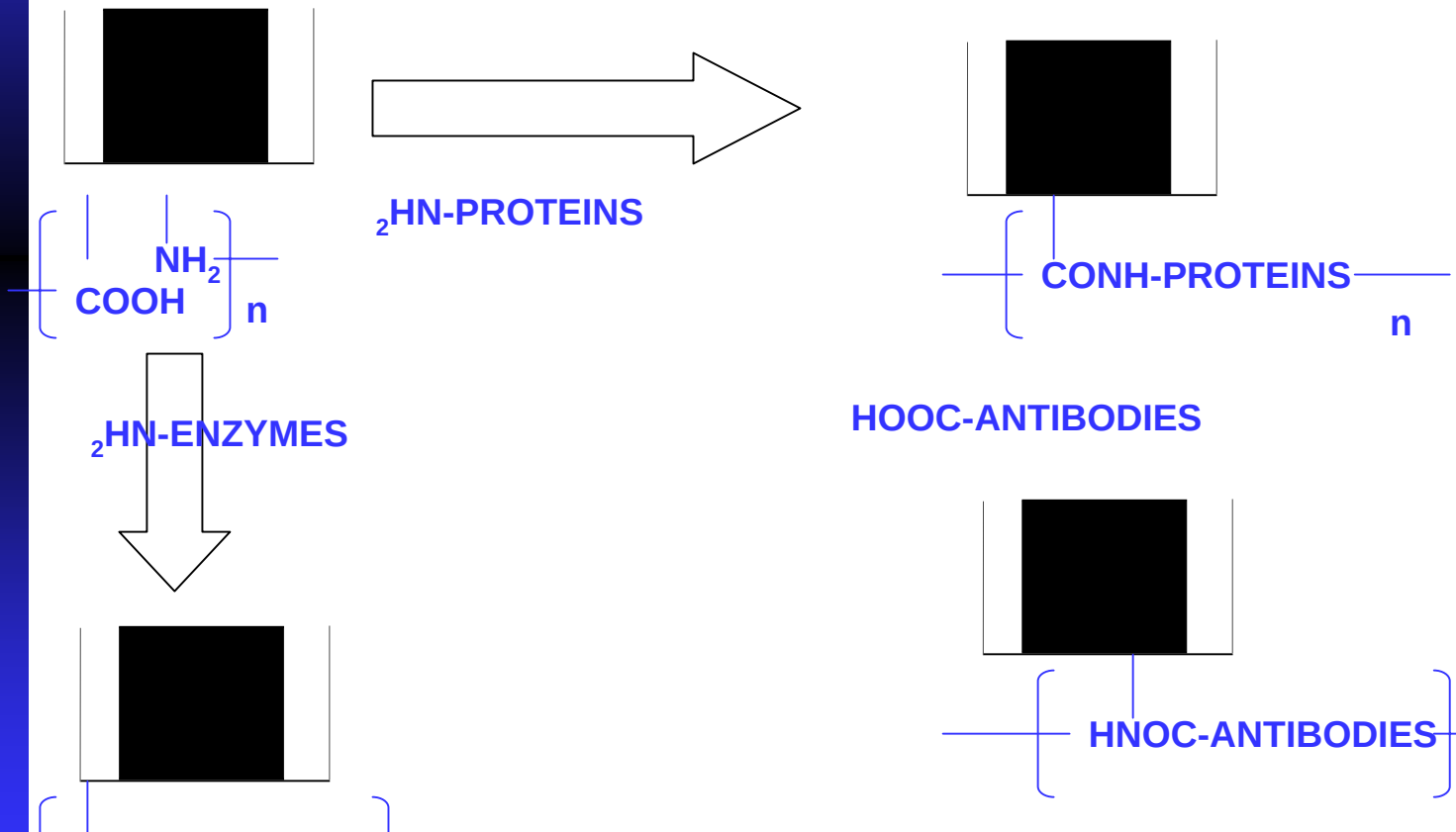


Selective Removal of Copper

PGN oxidation	% Cu Removed	RSD	Other Metals removed	% Metal Removed
10s	34.72	10.46	Mn	34.45 ±13.35%
100s	75±4.1%	5.47%	Zn	14.75 ±13.45%
200s	83.9±16.1	19.19%	Cu	99.1% ±40.3%
500s	99.7 ±0.3	0.003%		

Biosensing Applications





Summary

- Rapid, simple and convenient method of synthesizing Au nanoparticles in organic medium by the use of PAA which acts both as a reducing and a capping agent.
- The process takes about 30 min and the gold particles are stable and can be well dispersed or agglomerated depending on the concentration of the reactants.
- The potential of the PAA-metal nanoparticle films in the analysis and removal of heavy metals from aqueous medium is demonstrated
- Other metals salts of Co(II), Pd(II) and Ag(I) can also form metal nanoparticles on reduction with PAA and applied potential
- Preliminary applications for metal testing evaluated

Further Work

- Investigate the reduction of other metal salts with PAA
- Investigate the use of these metal nanoparticles in environmental and other applications

Acknowledgements

Bill Blackburn - Geology Department
Deborah Dittrich – Geology Department
Henry Eichelburger – Biology Department