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Surface Science Lab

表面增強拉曼光譜之應用
Application of Surface-Enhanced Raman Scattering

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General concept

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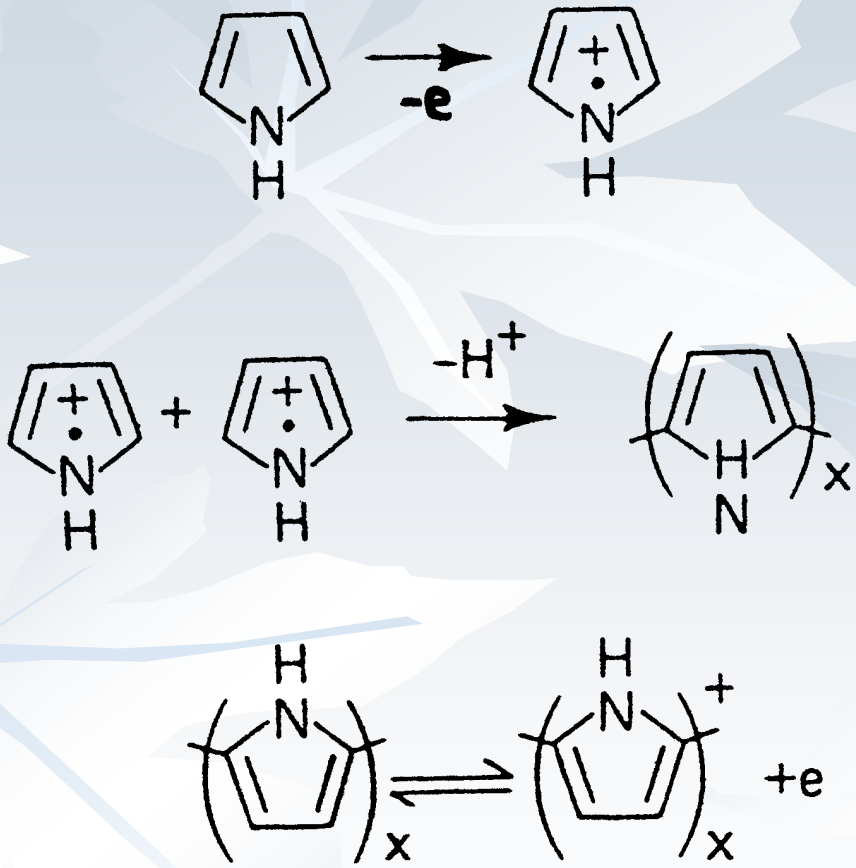
- Strongly SERS-active metal nanoparticles
  * Ag (488 or 514 nm laser)
  * Au or Cu (633 nm laser)
- Weakly SERS-active metal oxidize nanoparticles
  * TiO2
- Enhancing Raman signal or reducing fluorescence interference

- Choosing laser with short wavelength for measuring thin film
- SERS technologies being generally applied to two systems of adsorbates (Rhodamine 6G) and deposited species (polypyrrole)

Introduction

- Conjugating conducting polymers, polypyrrole (PPy, C_4H_5N)
  * application in gas sensors, electrochromic devices and batteries
  * preparation by chemical or electrochemical oxidation in aqueous or in organic solvents with various electrolytes
  * conducting property being attributed to the electrons hopping along the polymer chains and across the interchains owing to the conjugating bond
  * conductivity of oxidized PPy can be promoted to a level of 10^3 S cm^{-1}
  * factors influencing the physical and spectroscopic properties, the nature of solvent, polymerization method and rate, deposition time, pH in solution, dopants



Radical cation

Polymerization

Oxidized PPy

FIGURE 2 The mechanism of formation of polypyrrole.

- Raman spectroscopy being an essential technique to evaluate the structure situation of PPy in various states
- Enhanced Raman
  * Resonance-enhanced Raman spectroscopy (RRS)
  * Surface-enhanced Raman scattering (SERS)
- SERS occurring on roughened metal substrates in principle provides a powerful means of obtaining vibrational information
- Mechanism of SERS:
  * Electromagnetic enhancement : resulting from an apparent increase in the Raman cross section
  * Chemical enhancement : concerning about the charge transfer on the adsorbate-metal surface

Three kinds of scattering

Stokes，anti-Stokes，and Rayleigh

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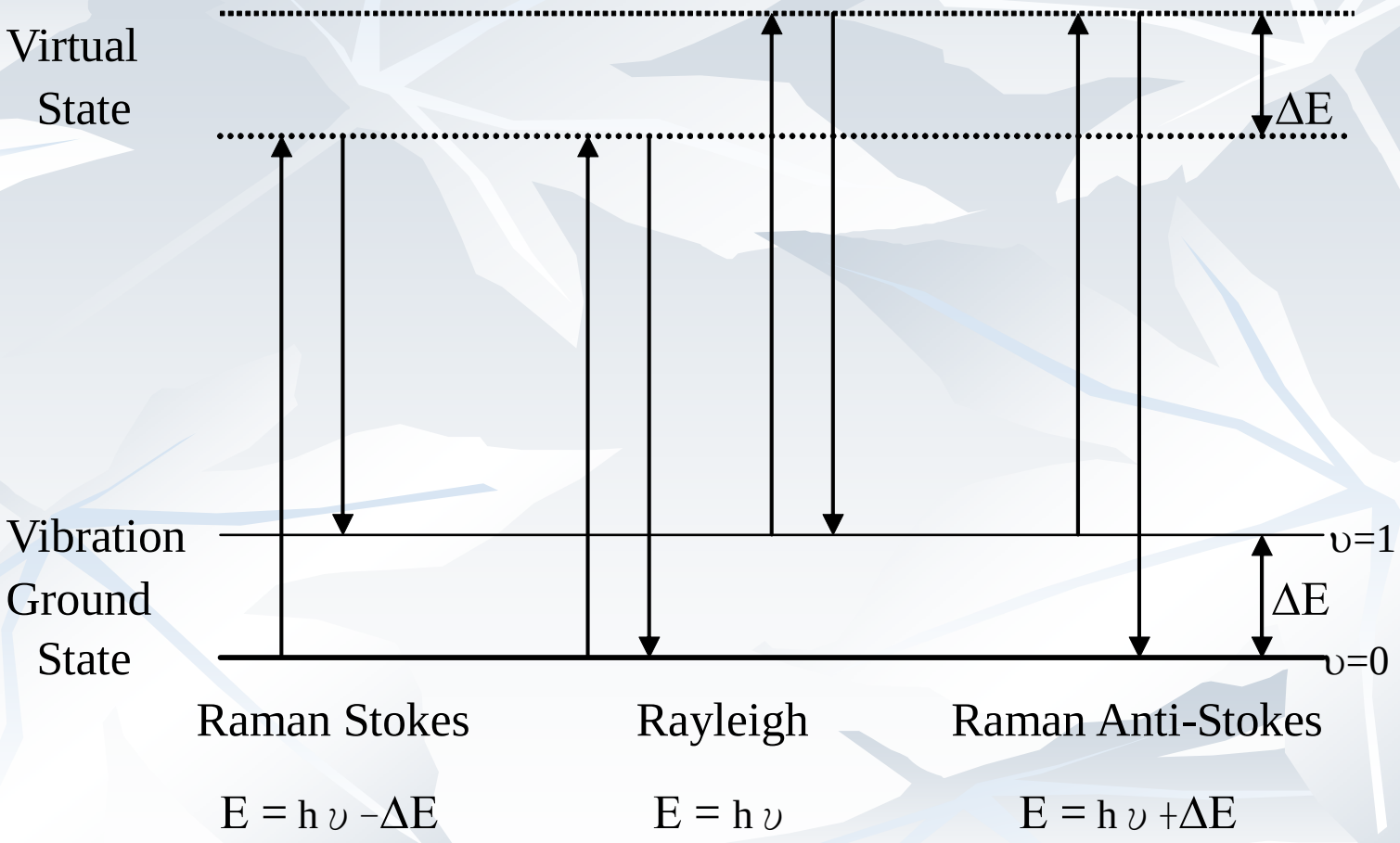


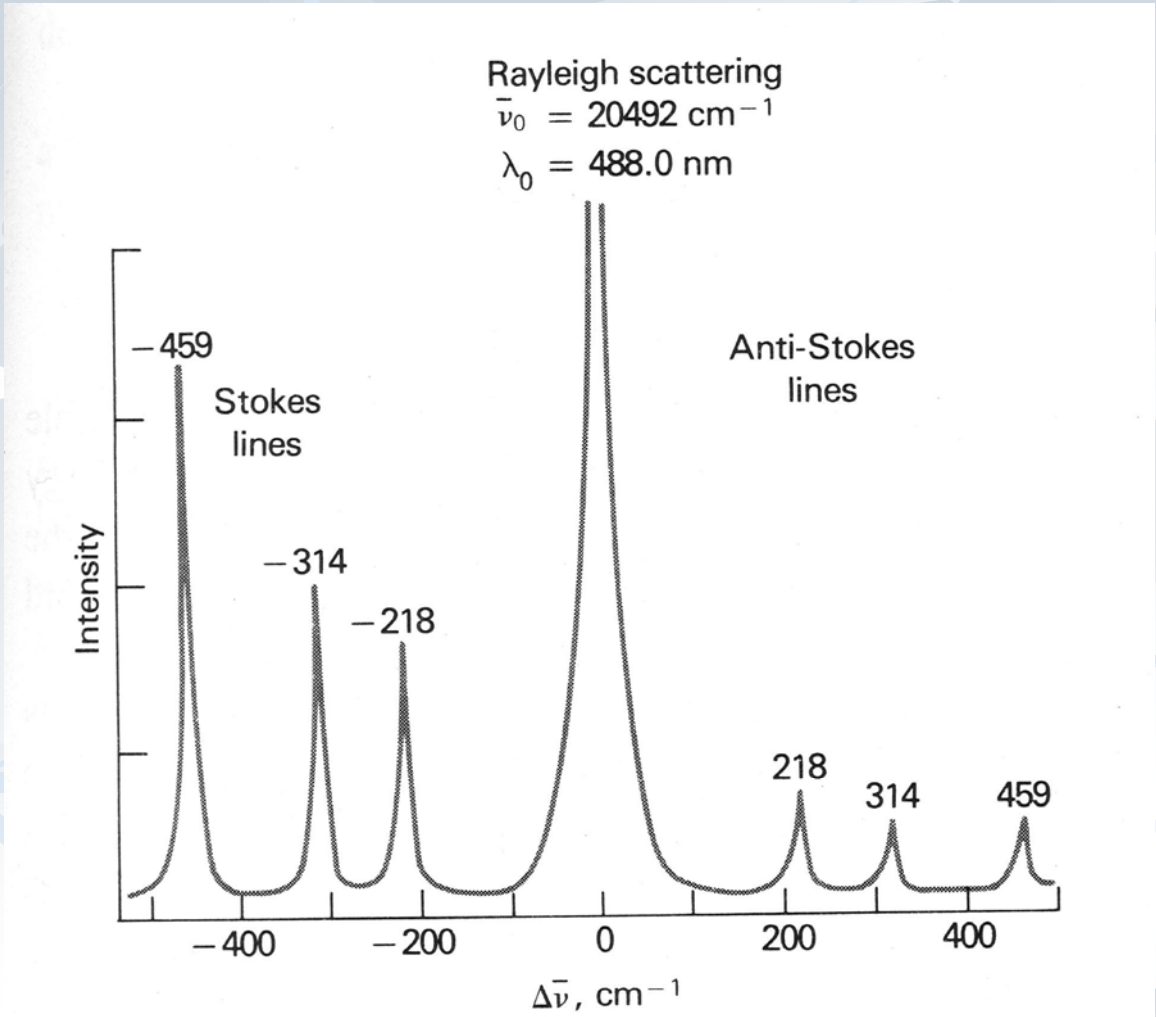


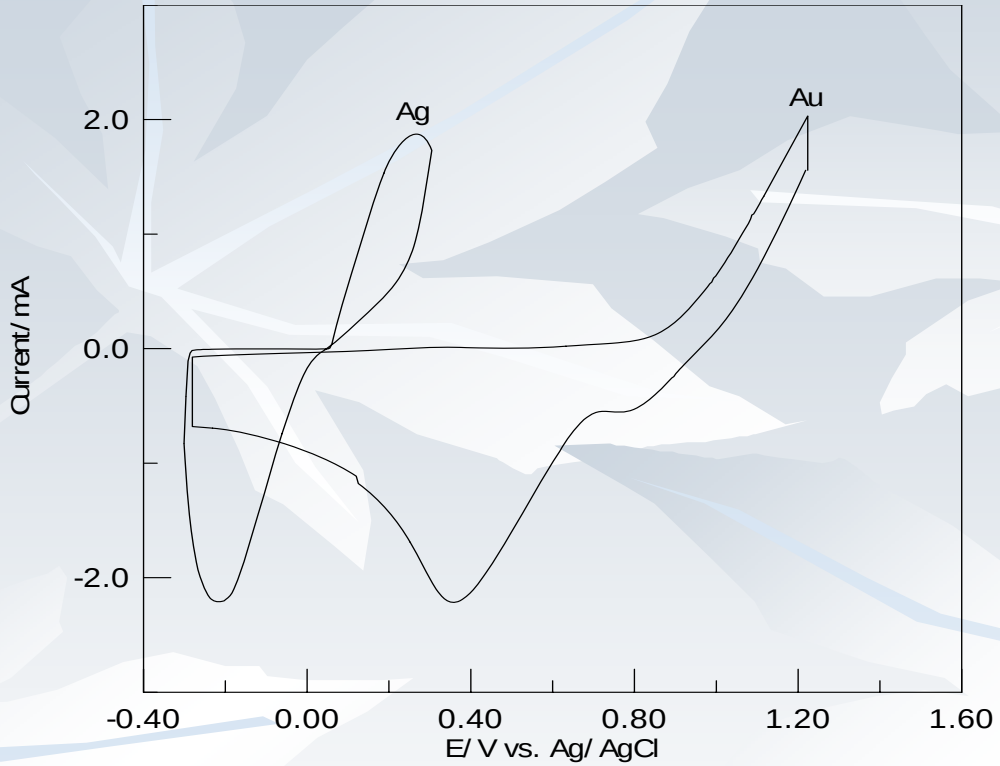
Figure 1 Raman spectrum of CCl_4 excited by the laser radiation of λo = 488 nm.

- Procedures of oxidation-reduction cycles (ORC)
  * Triangular-wave ORC
  * Square-wave ORC
- Advantage of Au substrate
  * Larger polarizable potential window of about of 2 V
  * Greater stability of SERS-active moieties
- Topics of this report
  * Characteristic SERS spectrum of PPy
  * Chemical interaction between deposited PPy and roughened Au substrate
  * New pathway for the autopolymerization of pyrrole on the Cl^- and Au-containing nanocomplexes
  * Other improved SERS
  * Thermal influences on SERS performances

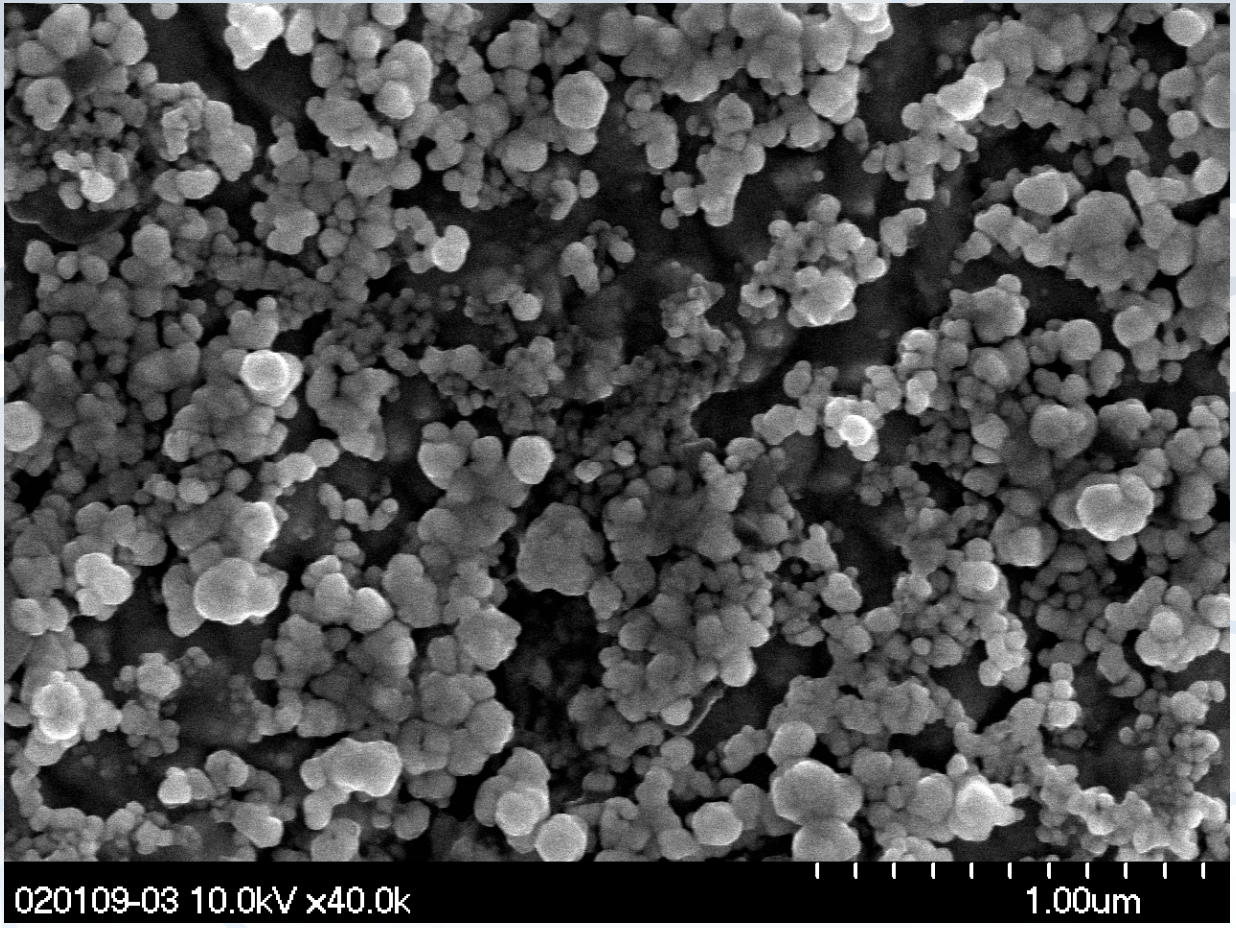
Experimental

- Roughening Au substrates
  * Before ORC, Au being mechanically polished as smooth as a mirror
  * Au being cycled in a aqueous solution containing 0.1 M KCl from -0.28 V (holding 10 s) to 1.22 V (holding 5 s) at 500 mV/s for 25 times
- Electrodepositing PPy films
  * PPy on roughened Au being carried out at a constant anodic potential of 0.85 V vs. Ag/AgCl in a aqueous solution containing 0.1 M pyrrole and 0.1 M $LiClO_4$
  * Charges used in depositing PPy being 500, 10 and 2 mC for XRD, SERS and XPS experiments

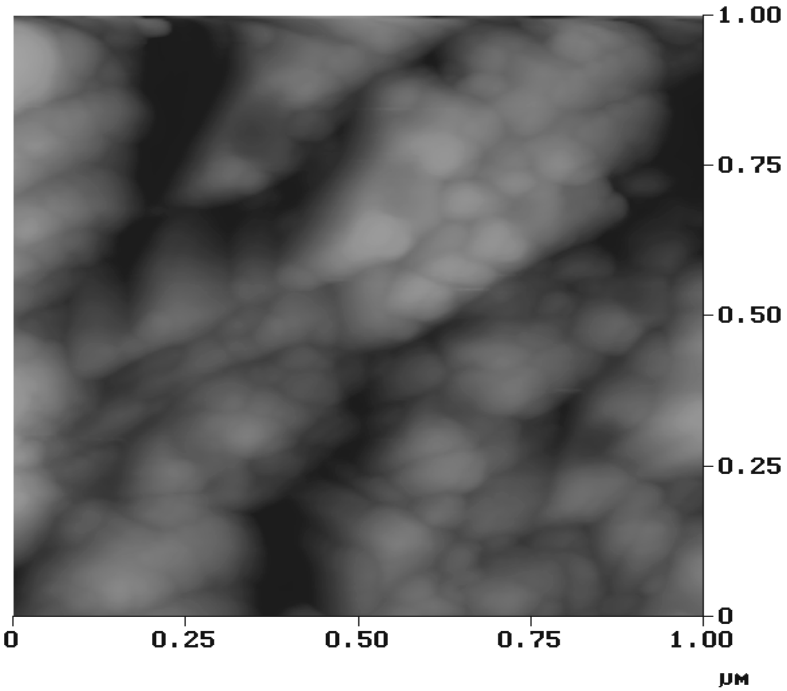
- Characteristics of PPy deposited on roughened Au
  * XRD (Model Dmax-B, Rigaku) : examining the orientations of gold substrates before and after roughening and PPy films
  * Raman spectra : using a Renishaw InVia Raman spectrometer employing a He-Ne laser operating at 632.8 nm of 1 mW and a charge couple device (CCD) detector with 1 cm^{-1} resolution
  * XPS measurements : a Physical Electronics PHI 1600 spectrometer with monochromatized Mg Kα radiation, 15 KV 250 W, and an energy resolution of 0.1~0.8% $\Delta E/E$ being used



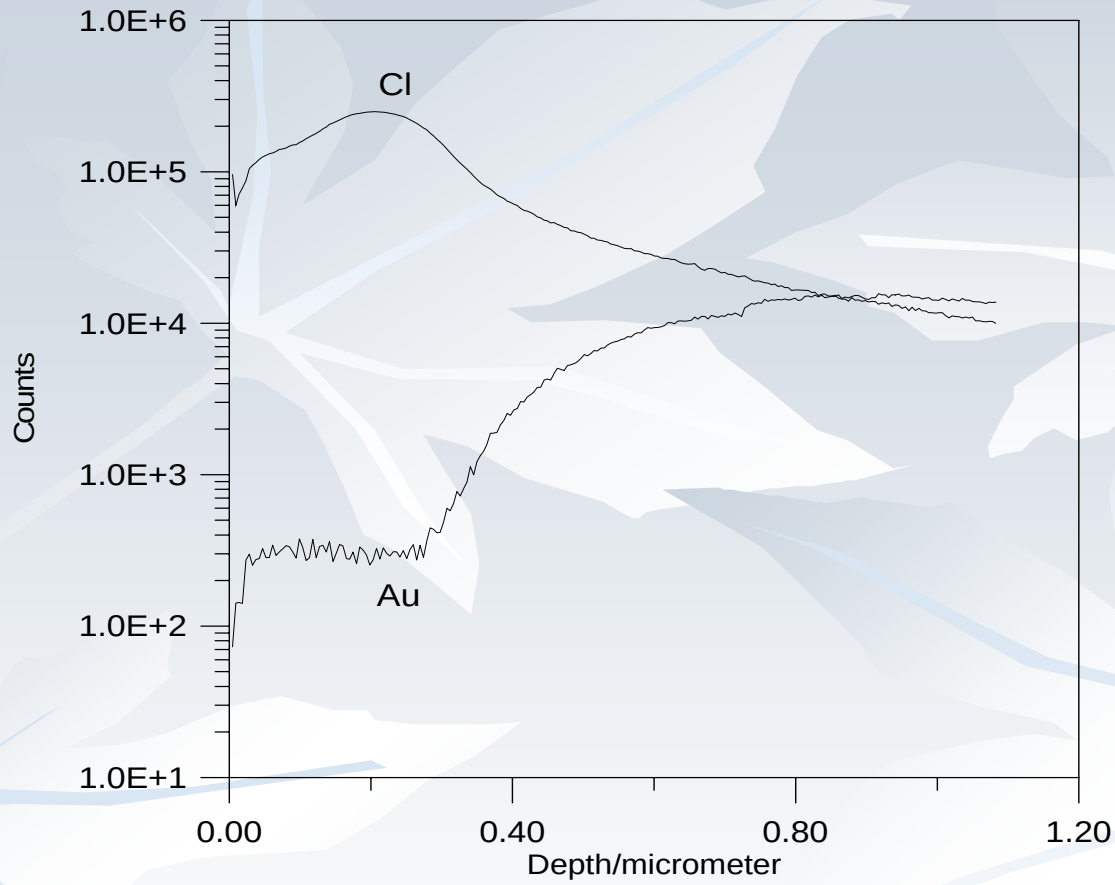
- Figure 1. Cyclic voltammograms at 500 mV/s of the 3rd scan for silver and gold electrodes in 0.1 M KCl
- Roughened Ag being unsuitable for depositing PPy on it at 0. 85 V vs. Ag/AgCl used in this study



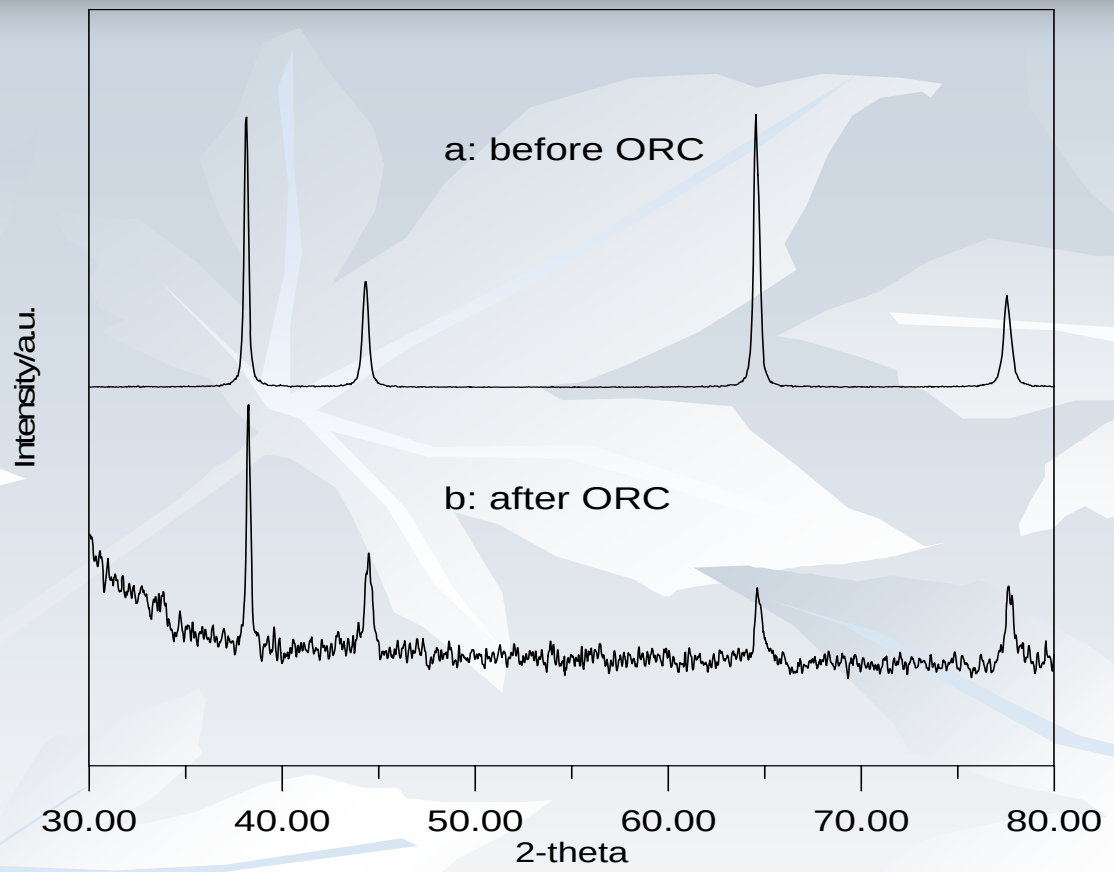
- Figure 2. SEM image of gold substrate after ORC treatment
- It is a typical aspect of a rough surface with a good Raman activity, demonstrating a microstructure smaller than 100 nm



- Figure 3. AFM image of gold substrate after ORC treatment
- The mean roughness of Au roughened with 0, 25 and 50 scans in ORC are 3.1, 145 and 113 nm, respectively

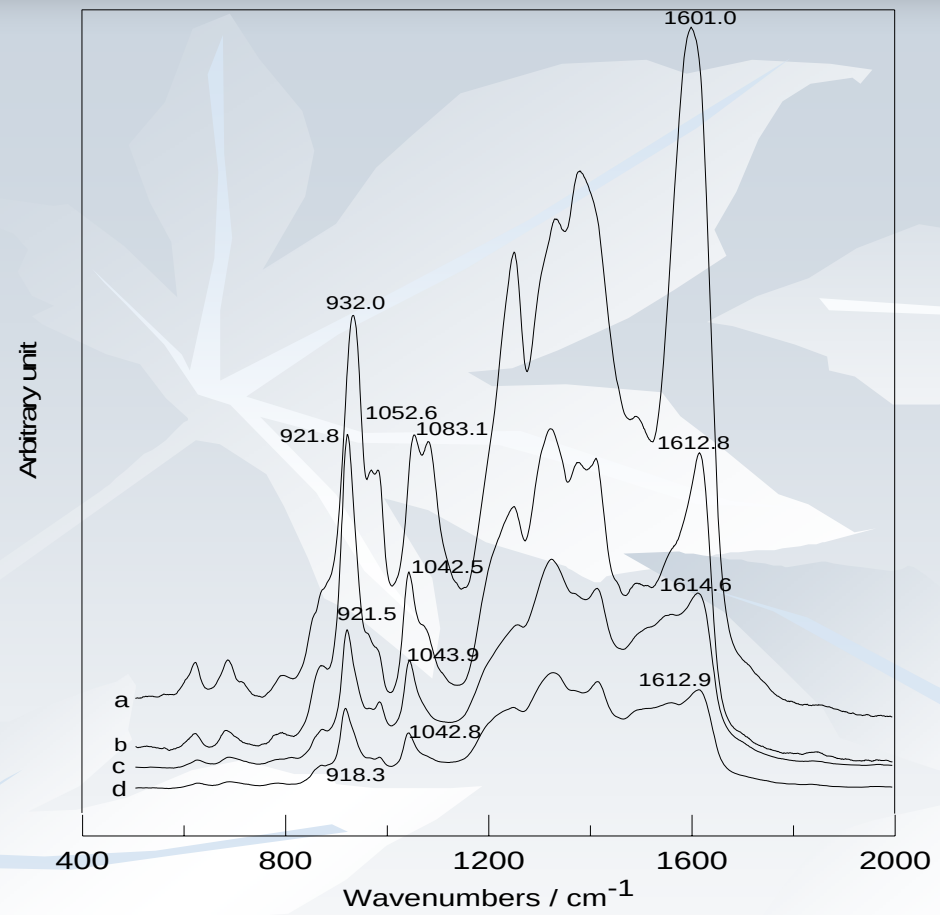


- Figure 4. Depth profile of Cl in Au-containing complex formed on the roughened Au substrate
- It reveals that the thickness of these complexes is ca. 0.5 μm



- Figure 5. XRD patterns of gold substrates before (pattern a) and after (pattern b) ORC treatments
- Peaks located at 38.2°, 44.4°, 64.6° and 77.5° being assigned to (111), (200), (220) and (311) faces of Au
- After ORC treatment, the (220) face of Au partly changes into the (111) face with the lowest surface energy

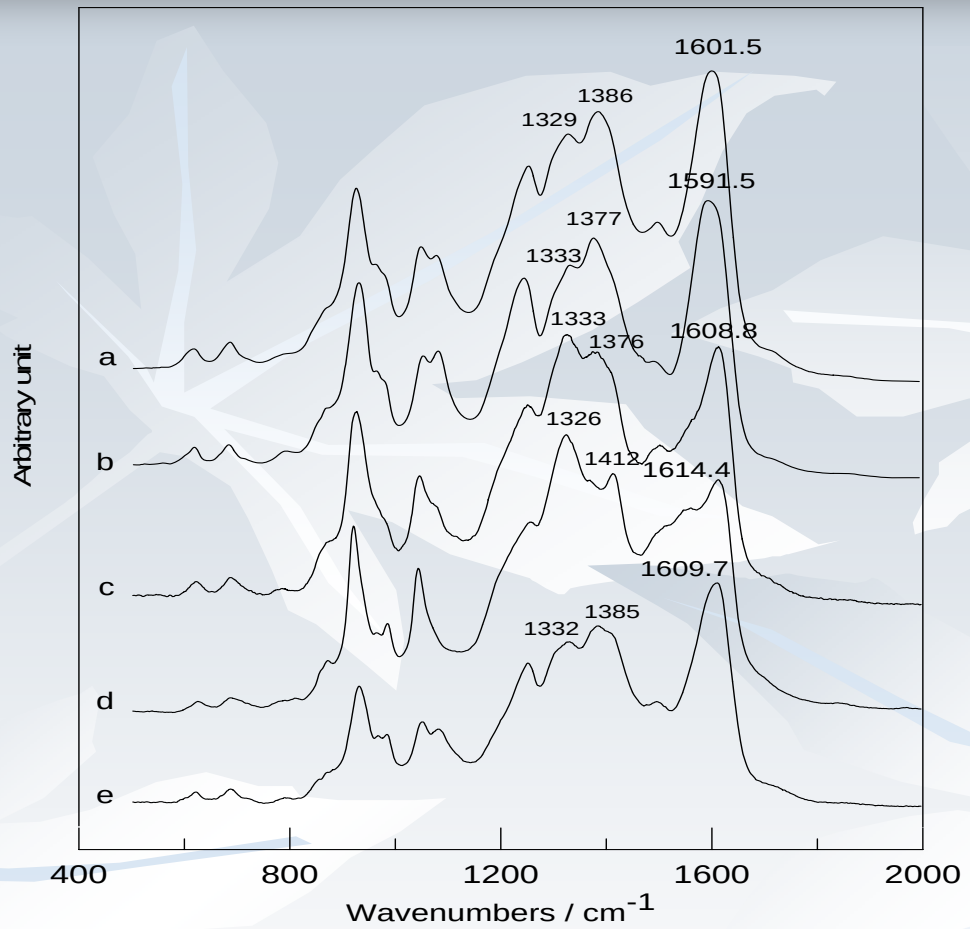
PART I



- Figure 6. SERS spectra of Raman double peaks of C-H in plane deformation in the range of 1000-1150 cm^{-1} of various PPy films prepared in aqueous solution. (a) oxidized PPy doped with ClO_4^- (sample 1). (b) water-treated PPy doped with ClO_4^- (sample 3). (c) fully reduced PPy (sample 4). (d) oxidized PPy doped with NO_3^- (sample 5)

Table 1. Performance of various PPy films on the conductivity and Raman peaks

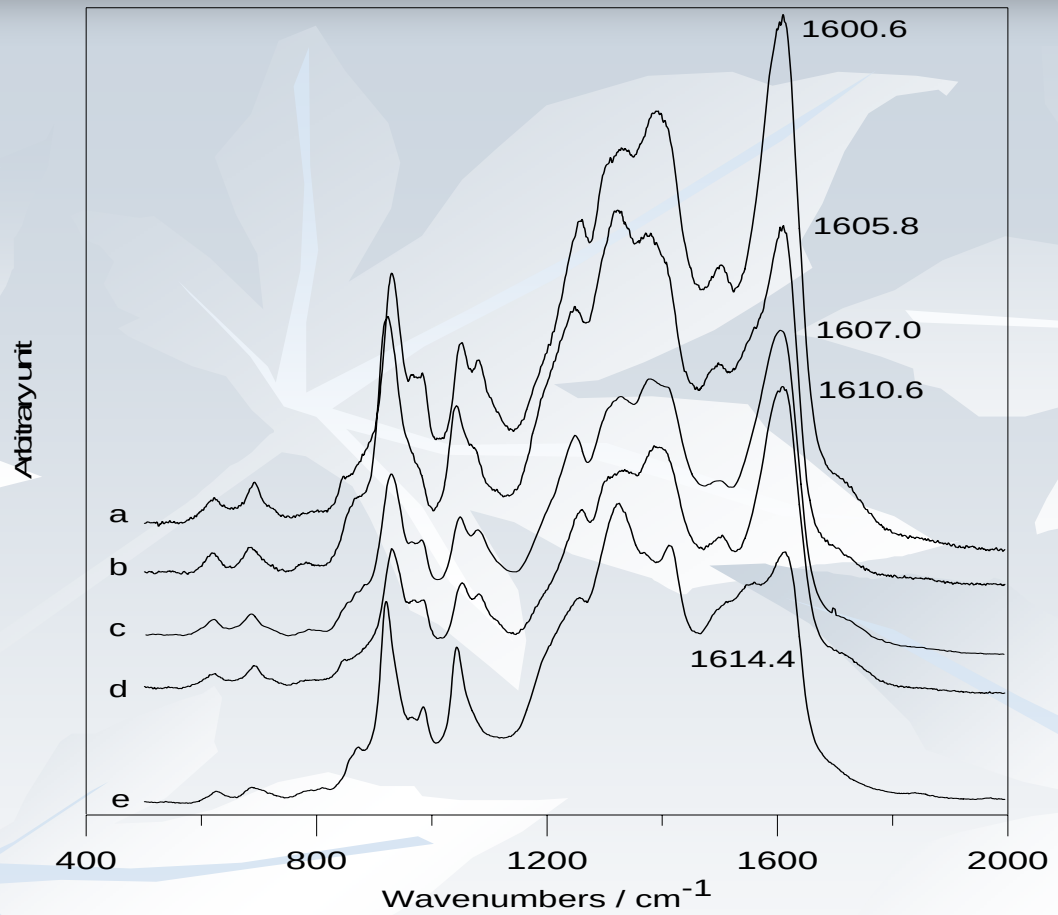
Sample	Conductivity/ S cm^{-1}	Raman peaks position of C-H in plane deformation		
		low frequency	high frequency	normalized relative intensity
1	71.9	1052.6	1083.1	0.96
2	303	1052.4	1082.8	1.08
3	27.2	1042.5	1082.4	0.44
4	0.014	1043.9	-	~0
5	3.6	1042.8	1082.3	0.21



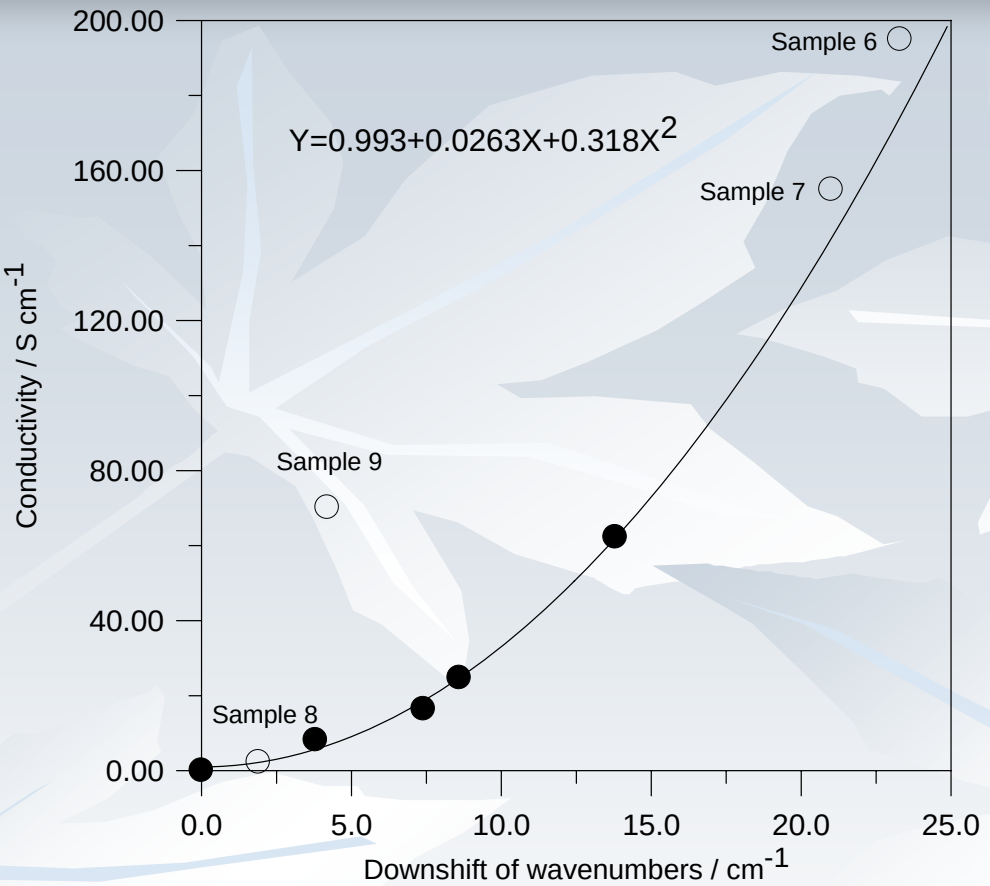
- Figure 7. SERS spectra of Raman double peaks of ring stretching in the range of 1300-1450 cm^{-1} of various PPy films. (a) Oxidized PPy prepared in aqueous solution (sample 1). (b) Oxidized PPy prepared in acetonitrile solution (sample 2). (c) Water-treated PPy (sample 3). (d) Fully reduced PPy (sample 4). (e) Over-oxidized PPy (sample 5)

Table 2. Performance of various PPy films on the conductivity and Raman peaks

Sample	Conductivity/ S cm^{-1}	Raman peaks position of ring stretching		
		low frequency	high frequency	normalized relative intensity
1	25.9	1328.8	1386.2	3.02
2	110	1332.6	1376.7	8.72
3	10.5	1332.6	1376.4	0.314
4	0.012	1326.3	1411.5	0.296
5	9.5	1332.1	1384.7	3.06

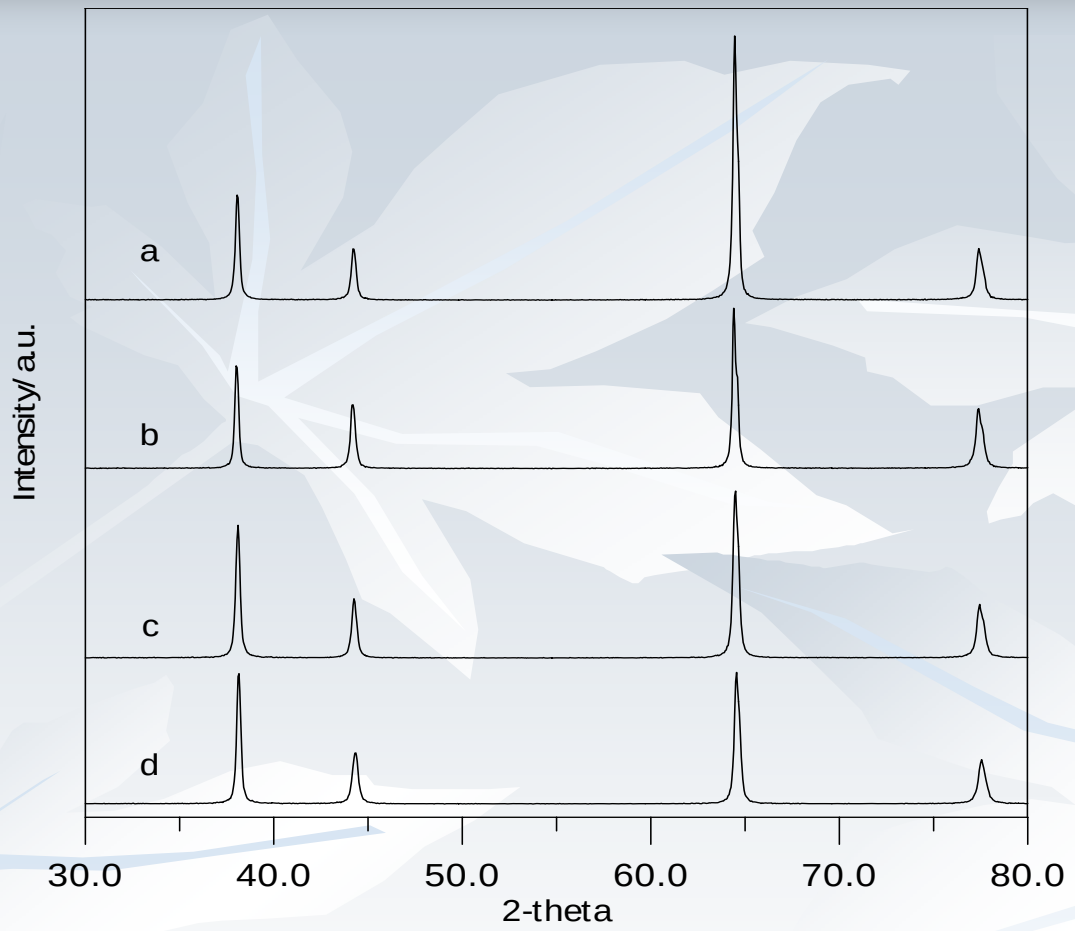


- Figure 8. SERS spectra of C=C backbone stretching at ca. 1600 cm^{-1} of various ClO_4^--doped PPy films. (a) Oxidized PPy (sample 1). (b) water-treated PPy (sample 2). (c) Over-oxidized PPy (sample 3). (d) Aged PPy (sample 4). (e) Reduced PPy (sample 5).

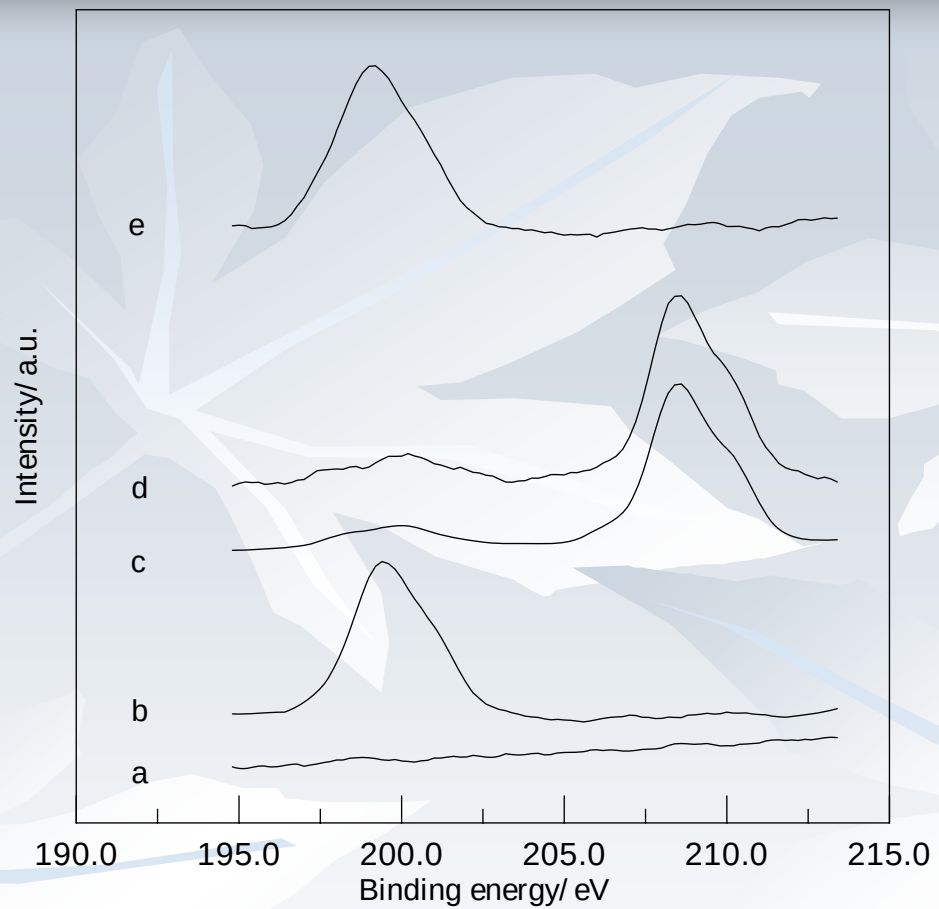


- Figure 9. Correlation of conductivities of various PPy-based films and their corresponding wavenumbers downshifts of Raman peak position of C=C bonds stretching from 1614.4 cm^{-1}. Solid circles (samples 1~5) were fitted to a polynomial expression. Hollow circles (samples 6~9) were used to examine this correlation. Sample 9: valence Cu-modified PPy

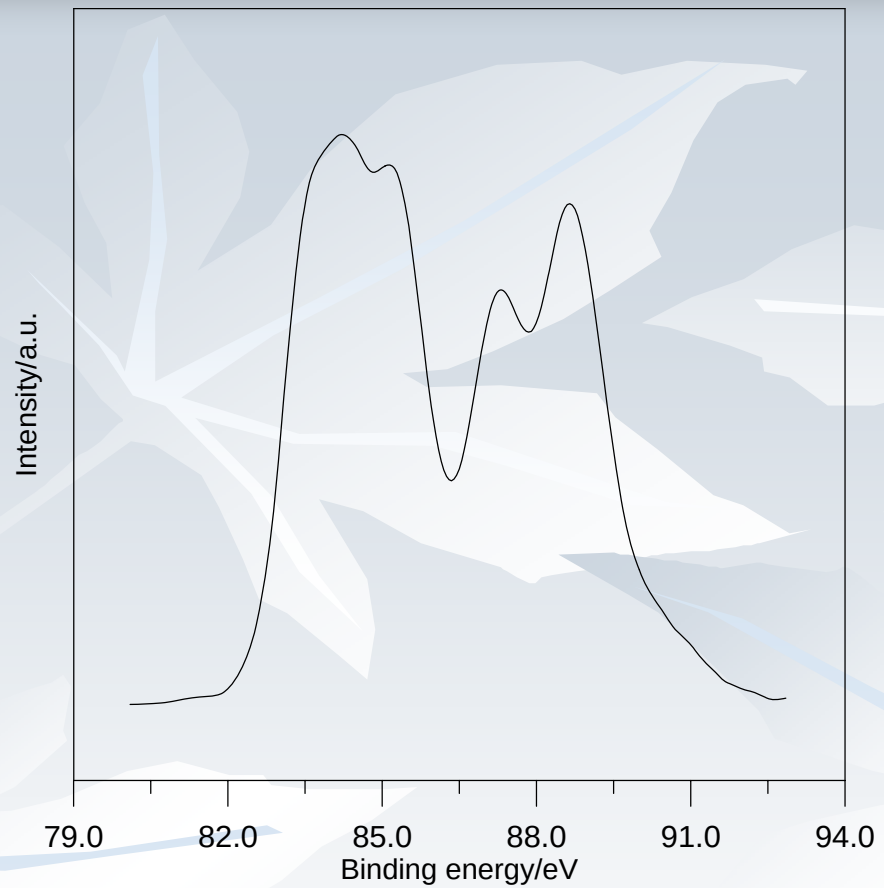
PART II



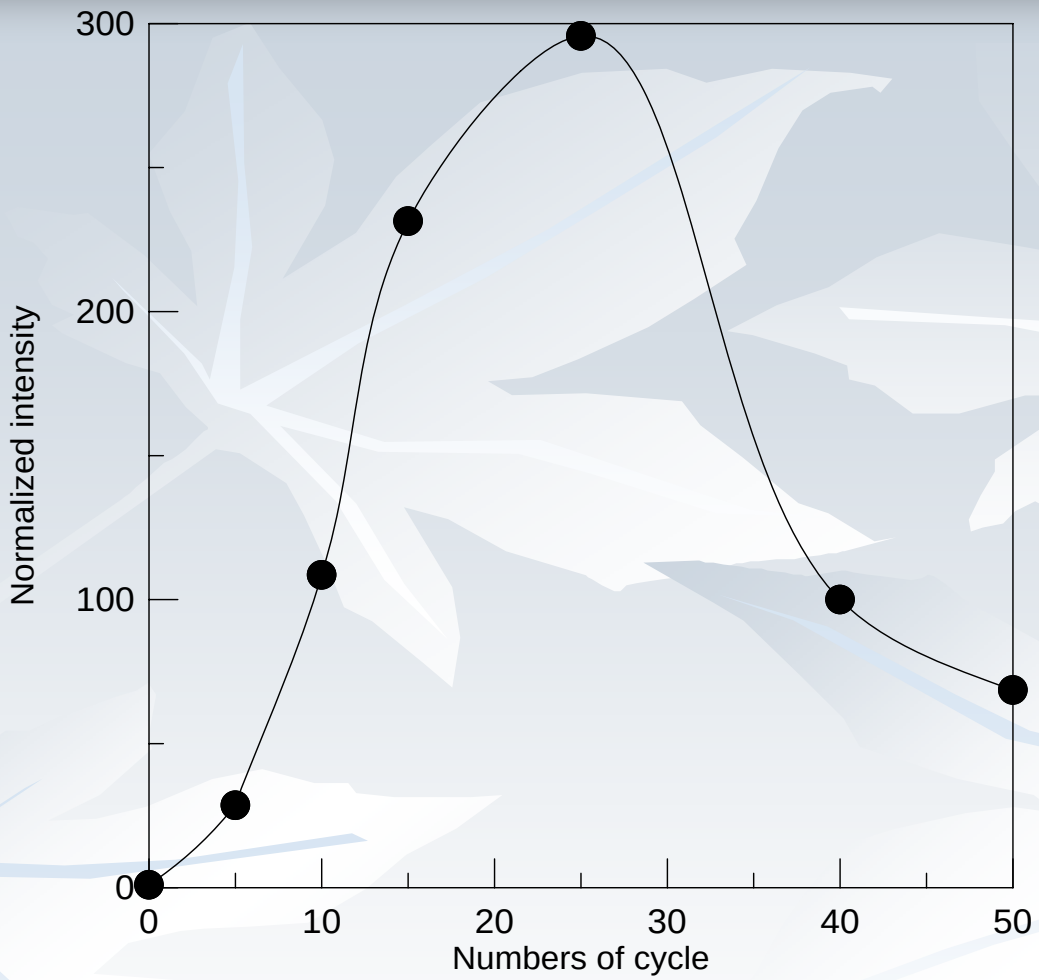
- Figure 10. XRD patterns of gold substrates before and after ORC treatments with different scans. Pattern (a) representing polished Au without further ORC treatment, patterns (b) ~ (d) representing Au roughened with 10, 25 and 50 scans, respectively.



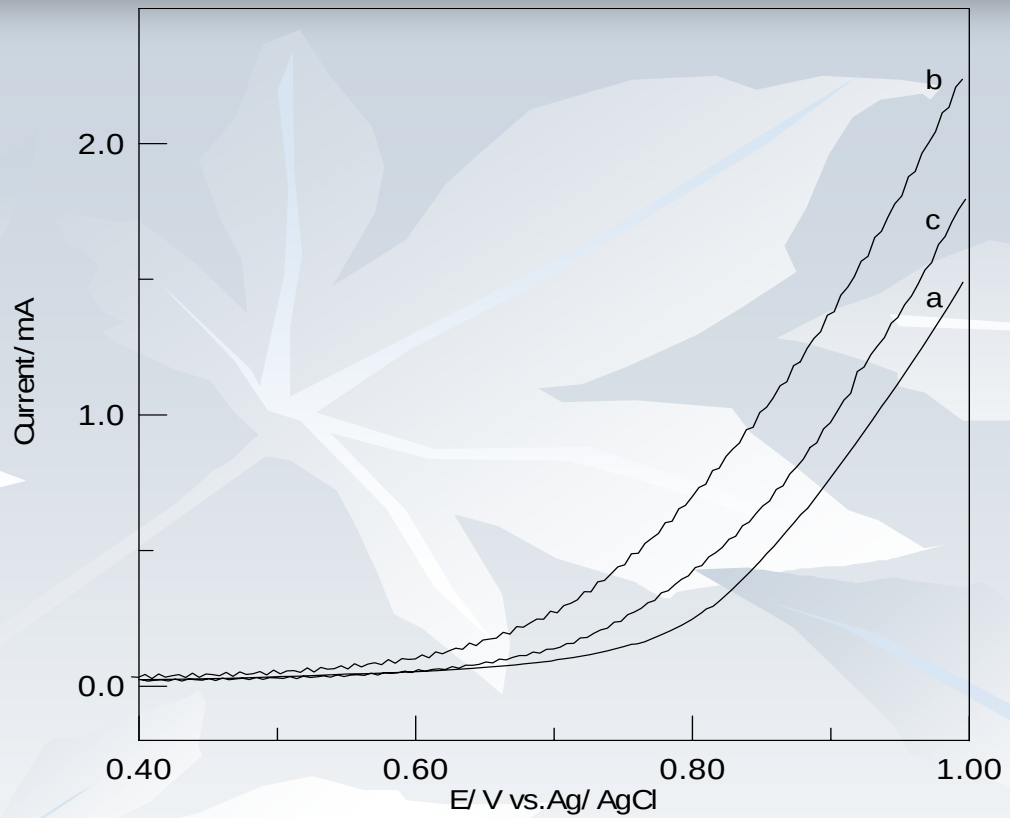
- Figure 11. XPS Cl 2p core-level spectra of Au substrates roughened with different scans in ORC. Curves (a) ~ (e) representing 5, 10, 15, 25 and 50 scans, respectively.
- Chloride peaks at 208 and 199 eV are assigned to Cl (+7) and Cl (-1), respectively.



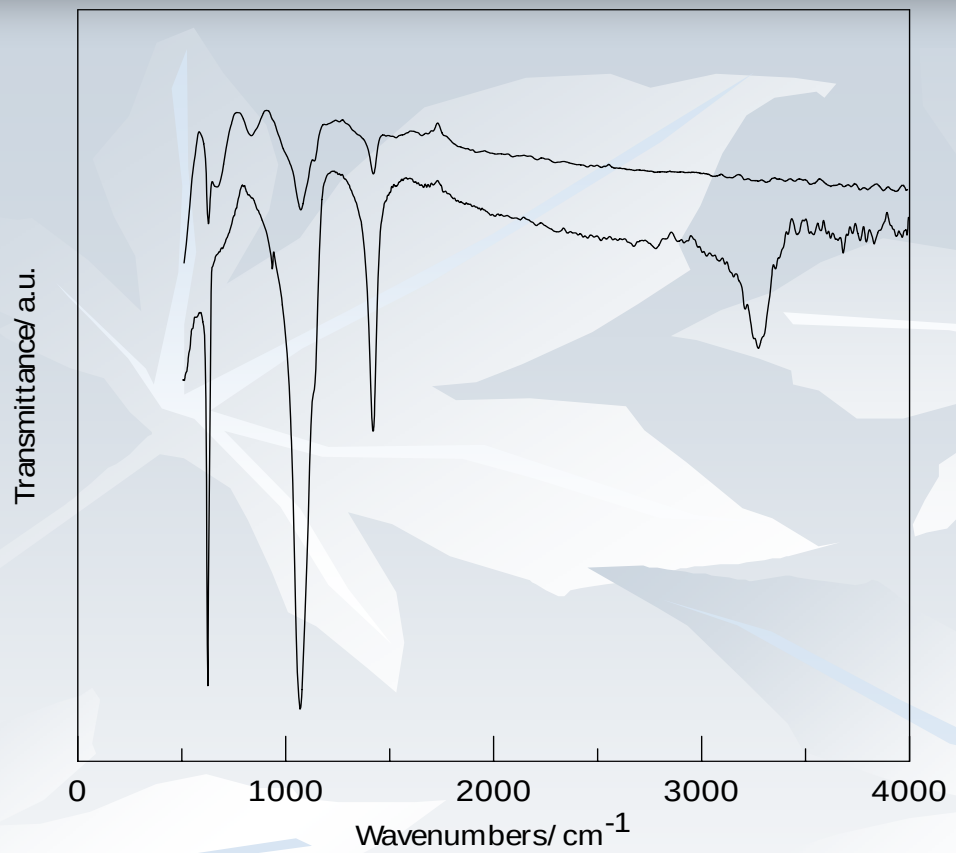
- Figure 12. XPS Au 4f7/2-5/2 core-level spectrum of the gold substrate with predominant (111) orientation roughened by ORC treatment of 25 scans.
- Complexes can be assigned to $Au(ClO_4)_4^-$ and $AuCl_4^-$ formed on the Au substrates.



- Figure 13. Normalized Raman intensity of PPy films deposited on Au substrates roughened with different scans in ORC.

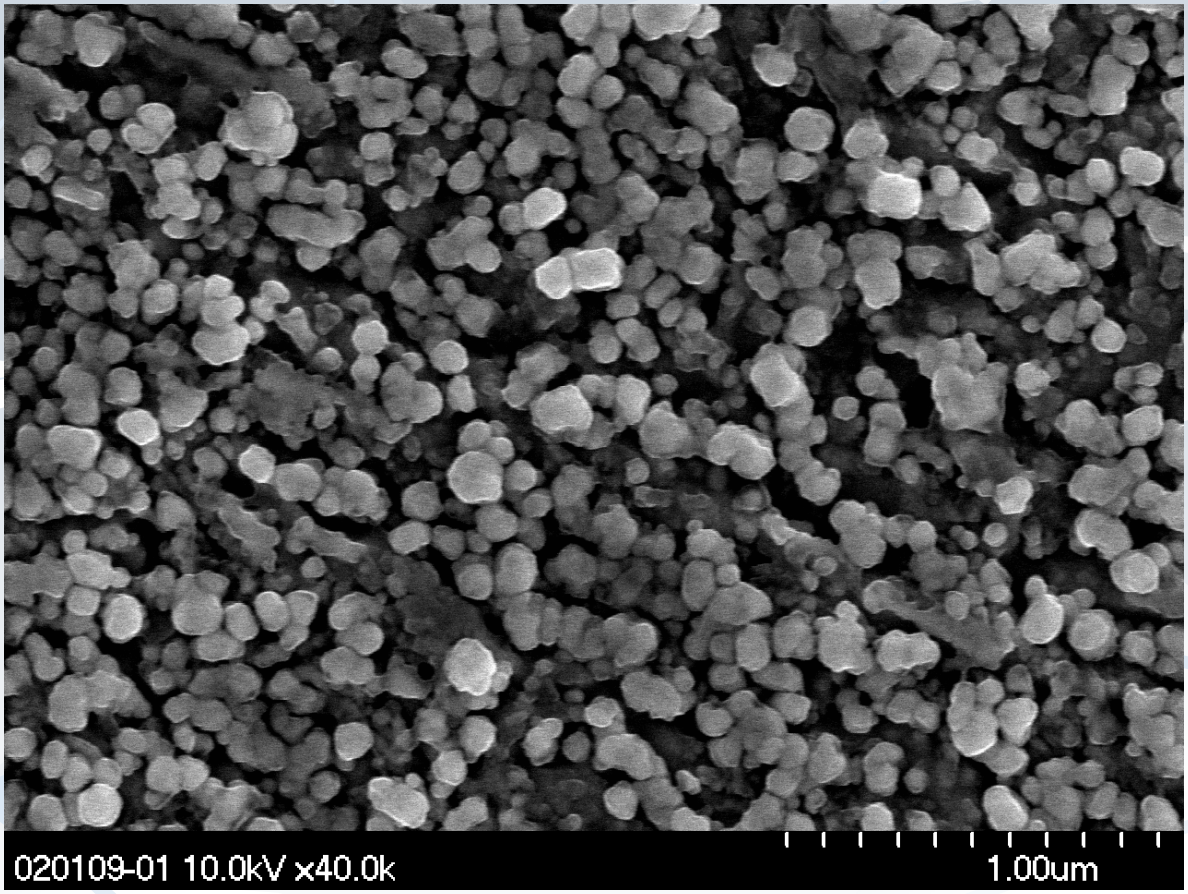


- Figure 14. I-E curves for pyrrole polymerized on Au substrates roughened with different scans in ORC. Curve (a) representing polished Au without further ORC treatment, curves (b) and (c) representing Au roughened with 25 and 50 scans, respectively.
- 0.8, 0.6 and 0.7 V vs. Ag/AgCl were the onset potentials of pyrrole polymerized on Au substrates roughened with 0, 25 and 50 scans in ORC, respectively.

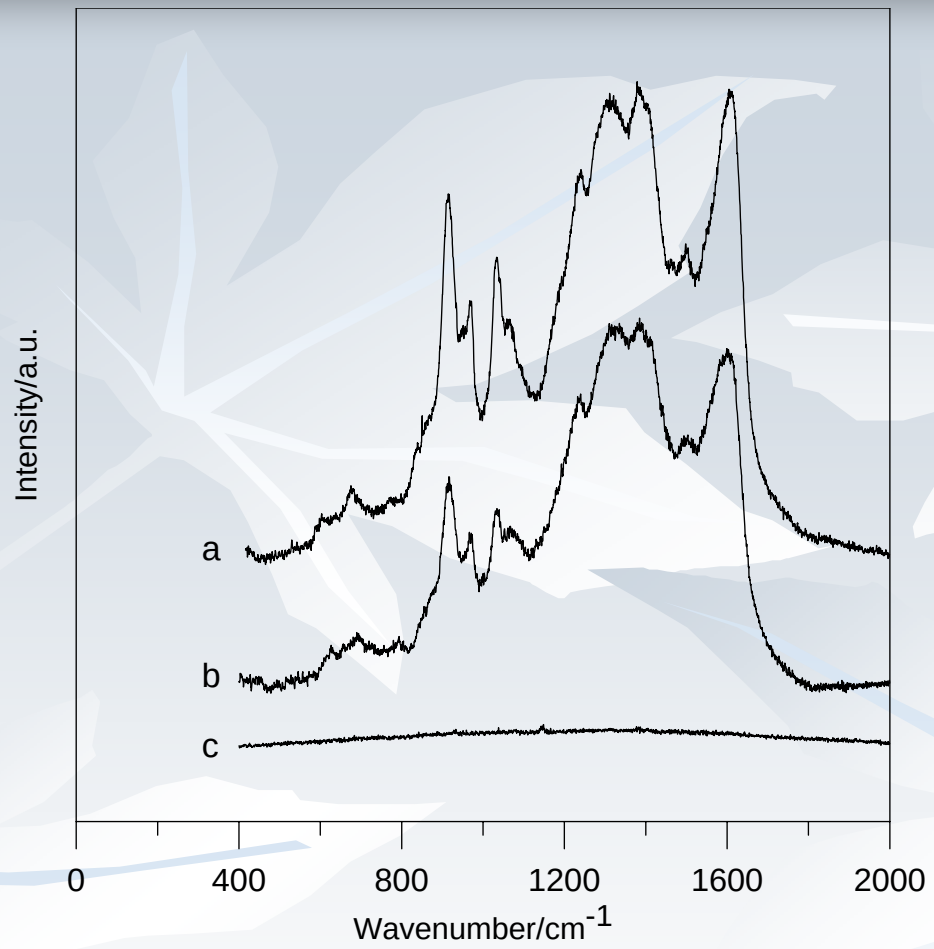


- Figure 15. FTIR spectra of PPy films deposited on polished Au (upper) and on Au roughened by ORC for 25 scans (lower), respectively.
- Broad peak, occurring at 3100-3400 cm^{-1} corresponding to the N-H stretching, markedly appears when PPy deposited on Au roughened with 25 scans in ORC.

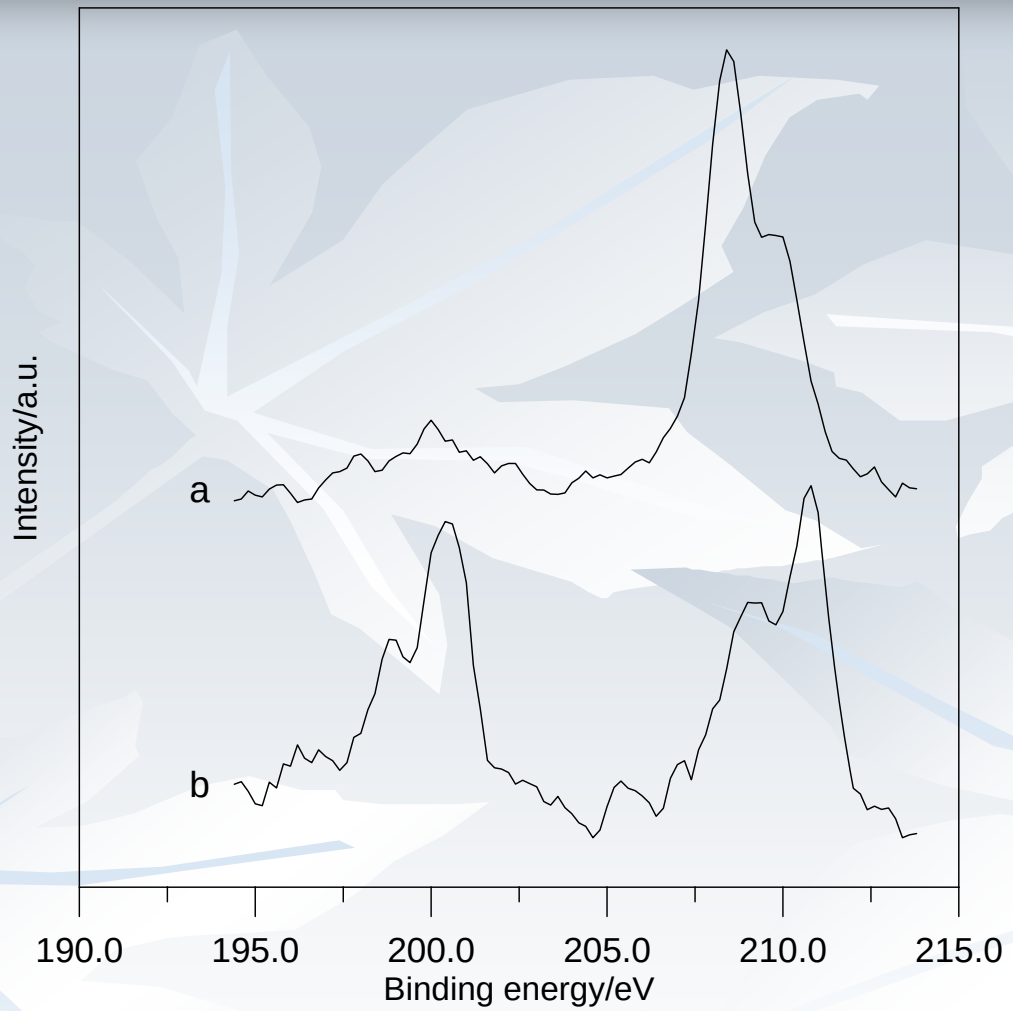
PART III



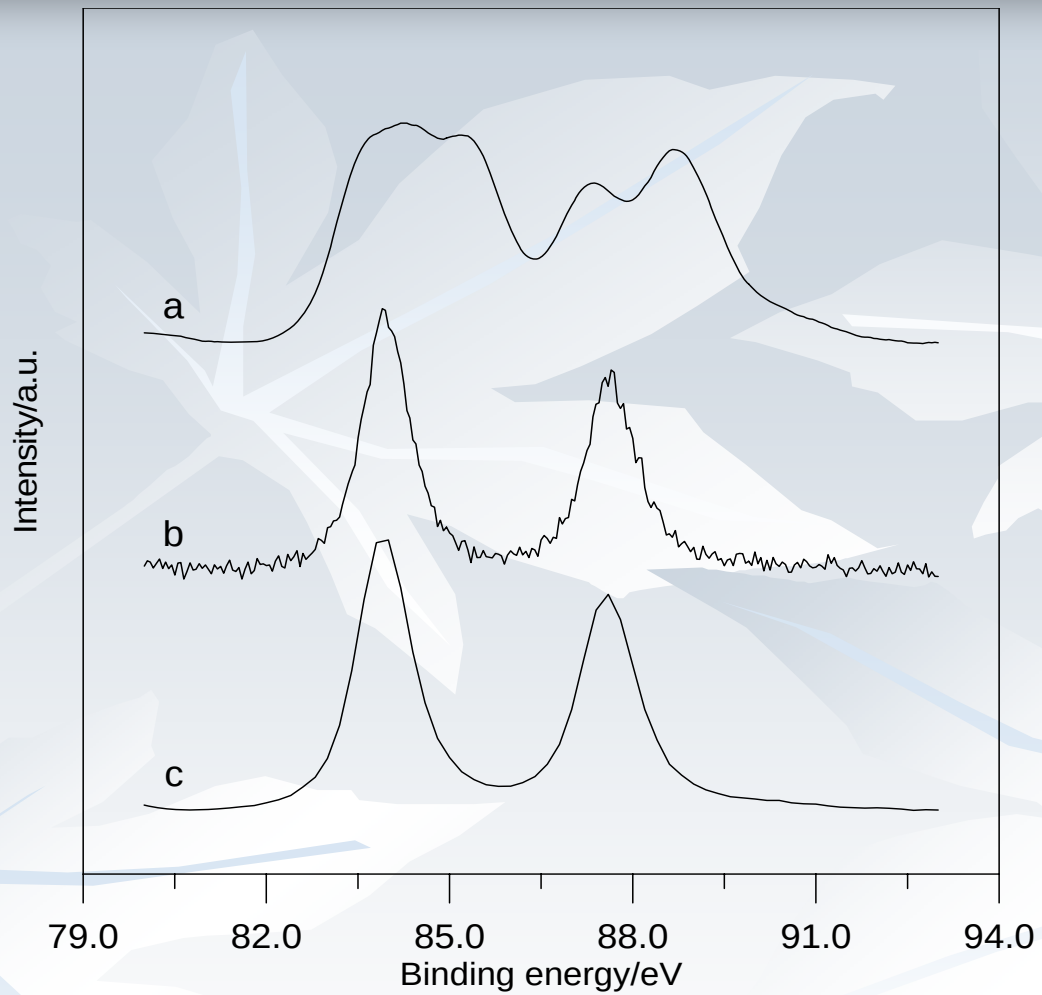
- Figure 16. SEM image of autopolymerized PPy film on roughened Au substrate due to its electrochemical activity of Cl and Au-containing complex



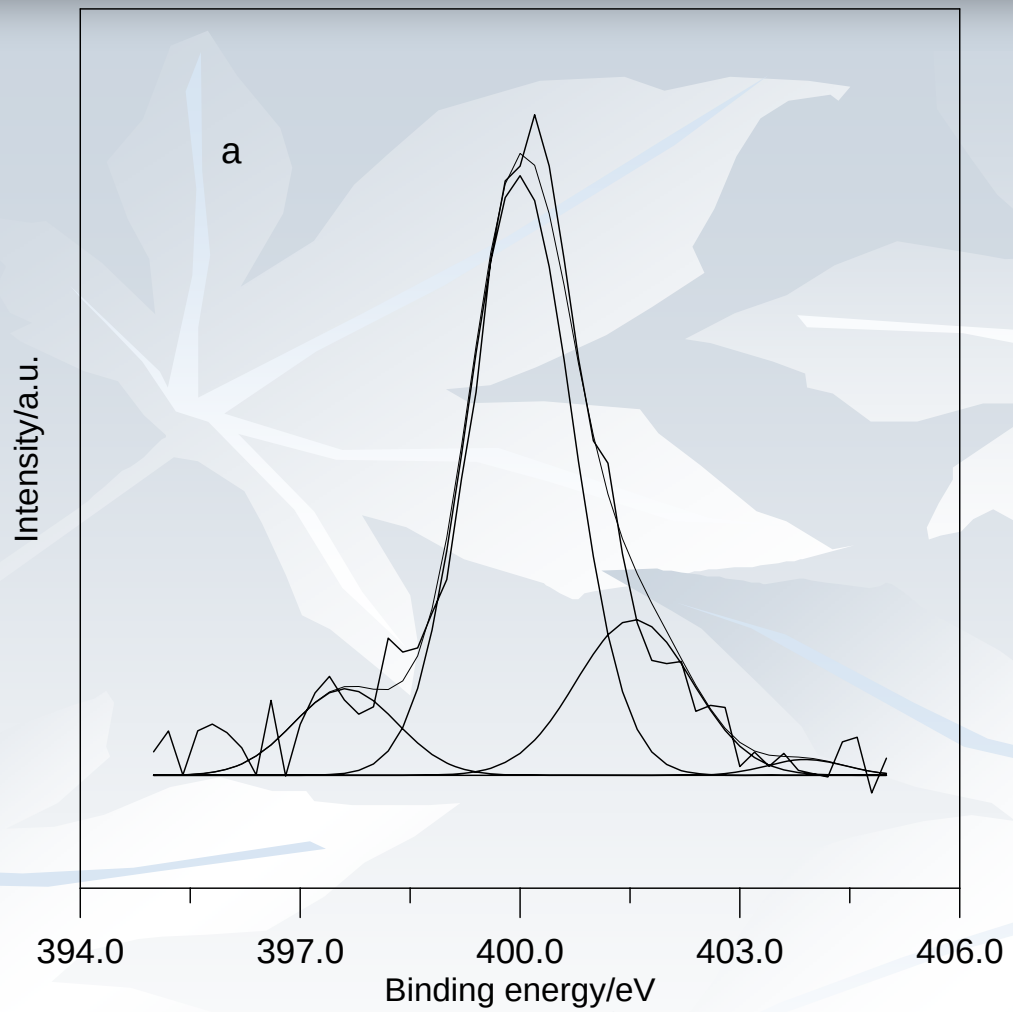
- Figure 17. Raman spectra of PPy films prepared with different methods on roughened Au substrates and pure pyrrole monomer on polished Au without further ORC treatment (curve c). Curves a and b represent autopolymerized and electropolymerized PPy films, respectively.



- Figure 18. XPS Cl 2p core-level spectra of the roughened Au substrates before (curve a) and after (curve b) the autopolymerization of PPy.



- Figure 19. XPS Au 4f7/2-5/2 core-level spectra of the roughened Au substrates before (curve a) and after (curve b) the autopolymerization of PPy. Curve c represents the polished Au without further ORC treatment.



- Figure 20. XPS N 1s core-level spectrum of autopolymerized PPy film
- Positively charged nitrogen (-$N^{+}H$-) species with the higher binding energy (BE) tail (BE>401 eV)

Autopolymerization of pyrrole monomer:

$$3Py + 2Au(ClO_4)_4^- \text{ (or } AuCl_4^-) \rightarrow 3PPy + 6H^+ + 2Au(s) + 8ClO_4^- \text{ (or } Cl^-) \quad (1)$$

Decomposition of ClO_4^-:

$$ClO_4^- \rightarrow Cl^- + 2\,O_2 \quad (2)$$

Oxidation of PPy:

$$PPy + Au(ClO_4)_4^- \text{ (or } AuCl_4^-, \text{ or } O_2\text{)} + ClO_4^- \text{ (or } Cl^-) \rightarrow$$

$$PPy+ \text{ doped with } ClO_4^- \text{ (or } Cl^-) + Au(s) \text{ (or } O^{2-}) \quad (3)$$

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Improved SERS

PART IV

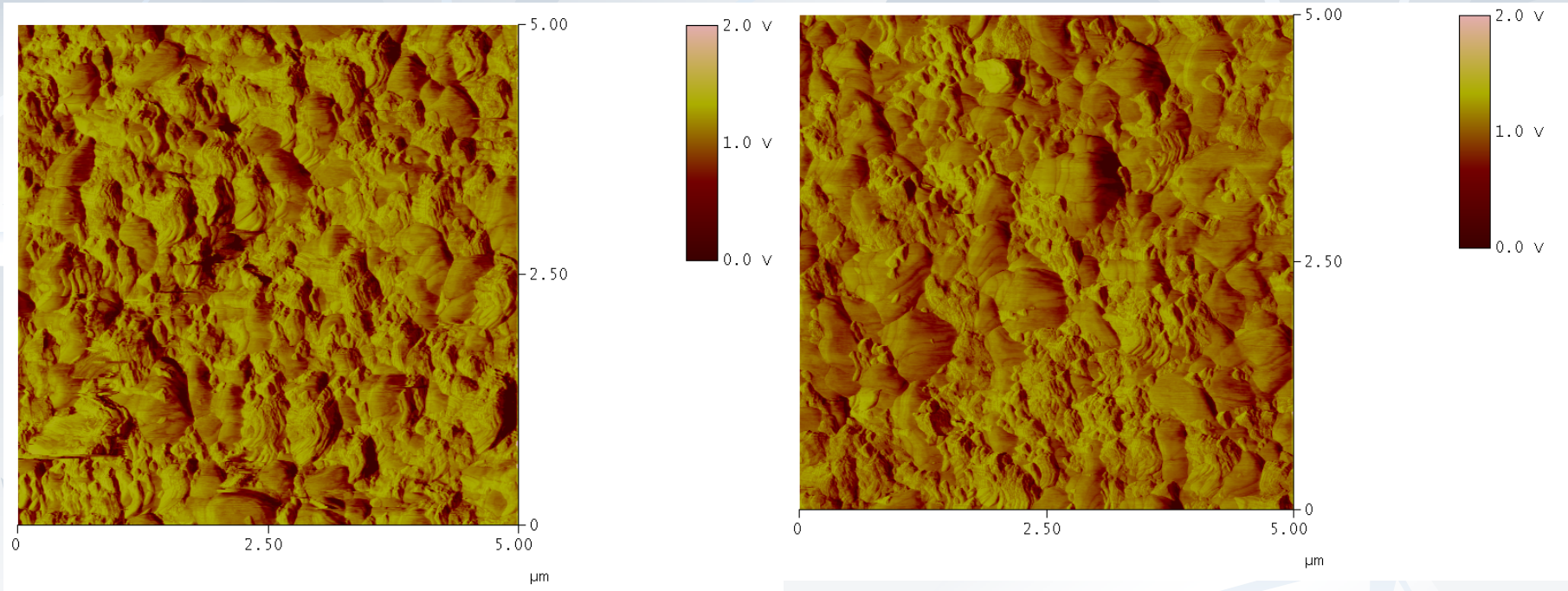
※ Sandwiched structure:
Au monolayers/PPy/roughened Au substrate

※ Effect of additives of TiO_2 nanoparticles in electrolytes in the ORC proceture

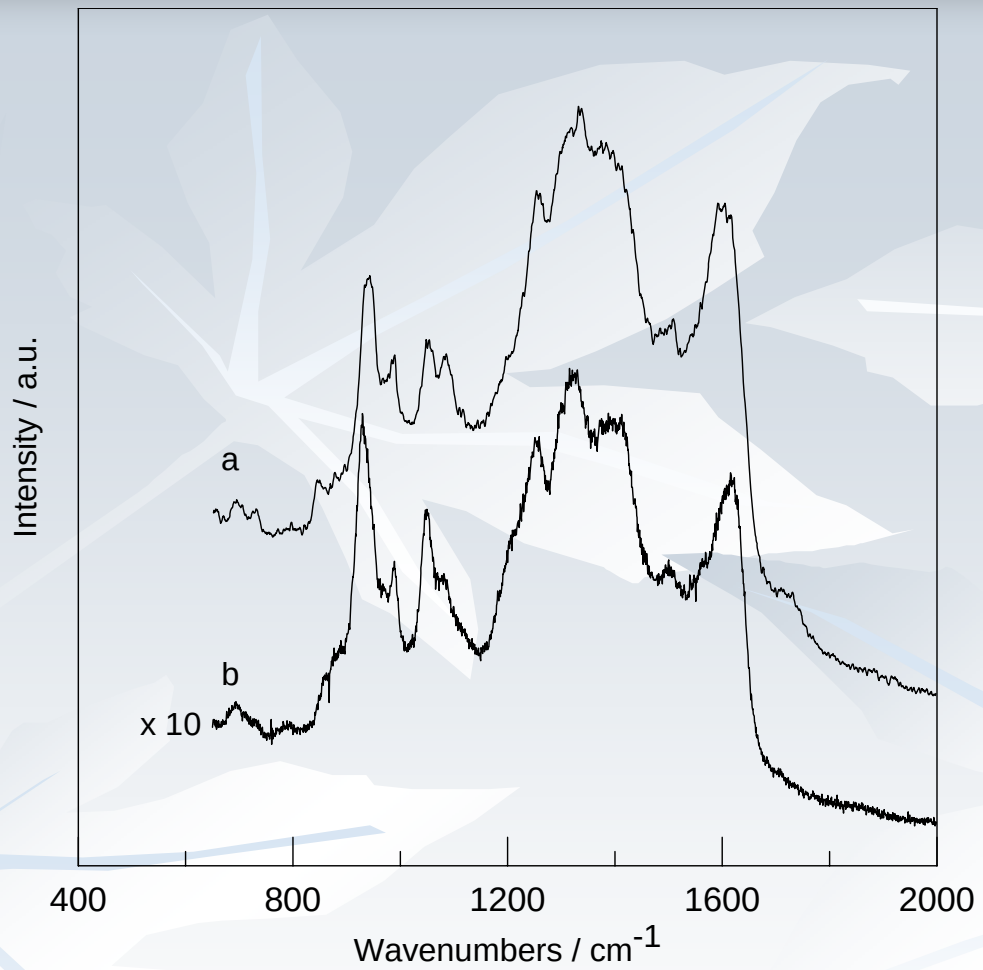
※ Au-Ag bimetallic roughened substrate

※ Effect of plasma treatment to Au substrate before and after the ORC procedure

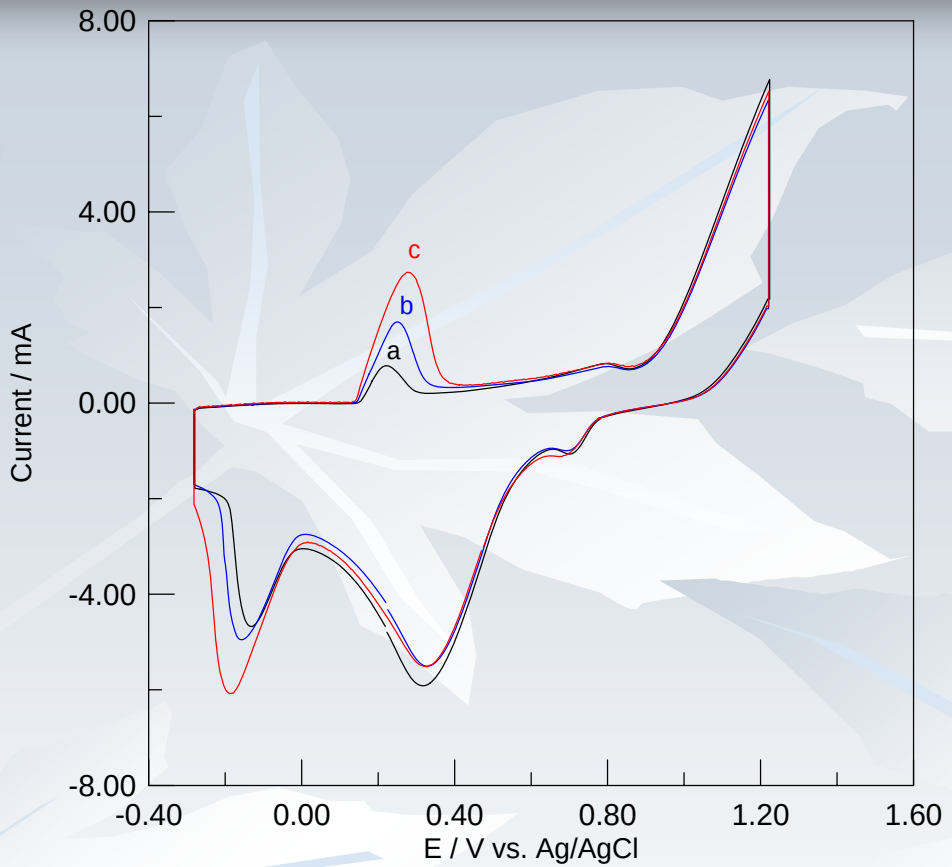
※ Optimum procedure-prepared Ag substrates



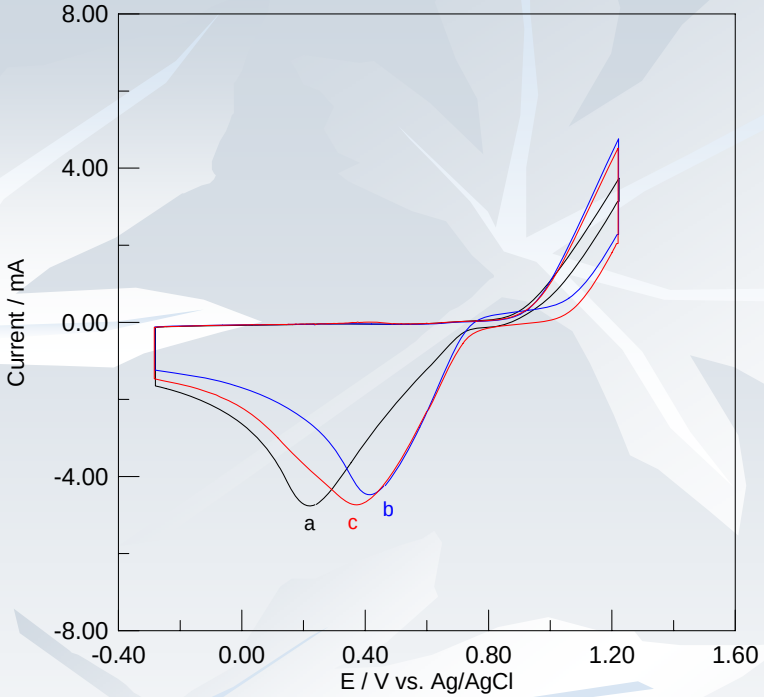
- Figure 21. AFM friction force images of PPy electrodeposited on roughened gold substrates with (left) and without (right) the coating with Au monolayers.
- The whole brightness is raised and the corresponding friction force is decreased due to the coating of Au monolayers on PPy

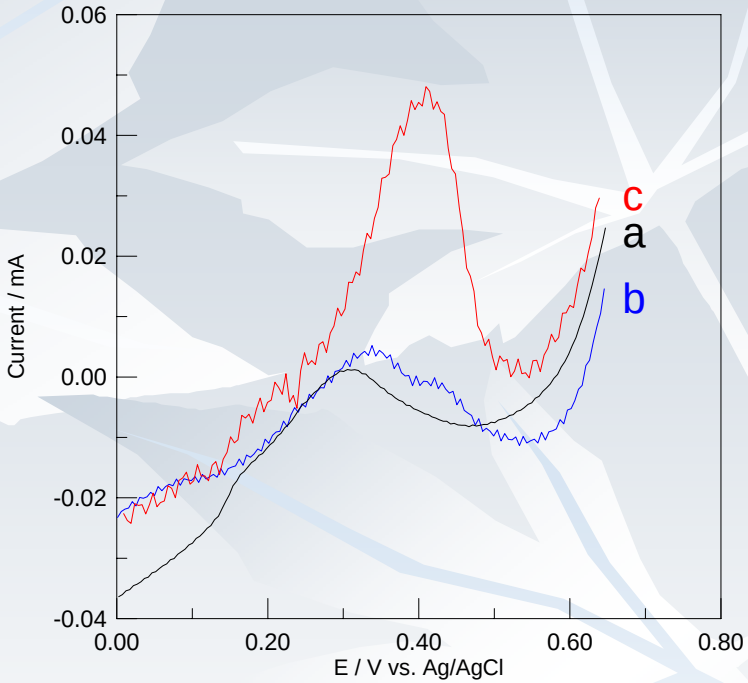


- Figure 22. SERS spectra of (a) PPy electrodeposited on roughened gold substrate and coated with gold monolayers and (b) PPy electrodeposited on roughened gold substrate; the intensity was magnified by 10-fold.

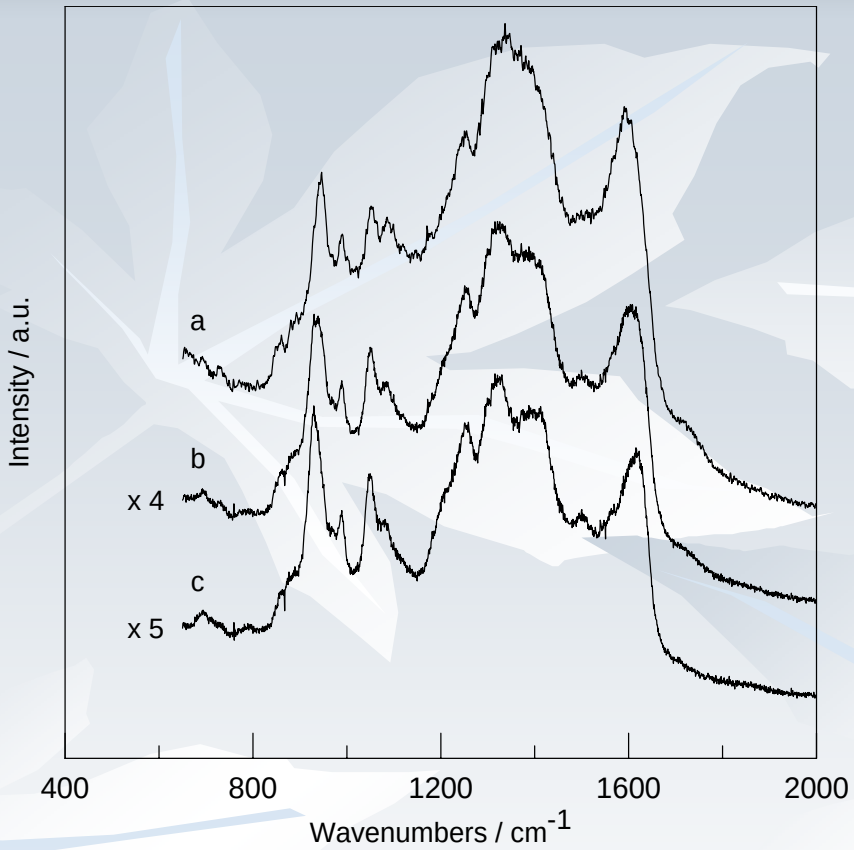


- Figure 23. Cyclic voltammograms at 500 mV/s of the 10th scan for electrochemically roughened gold substrates with predominant (111) orientation in different conditions. (a) In 0.1 M HCl. (b) In 1 mM TiO2 and 0.1 M HCl. (c) In 1 mM TiO2 and 0.1 M HCl, and irradiation with UV light of 4 W at 254 nm in the roughening procedure.

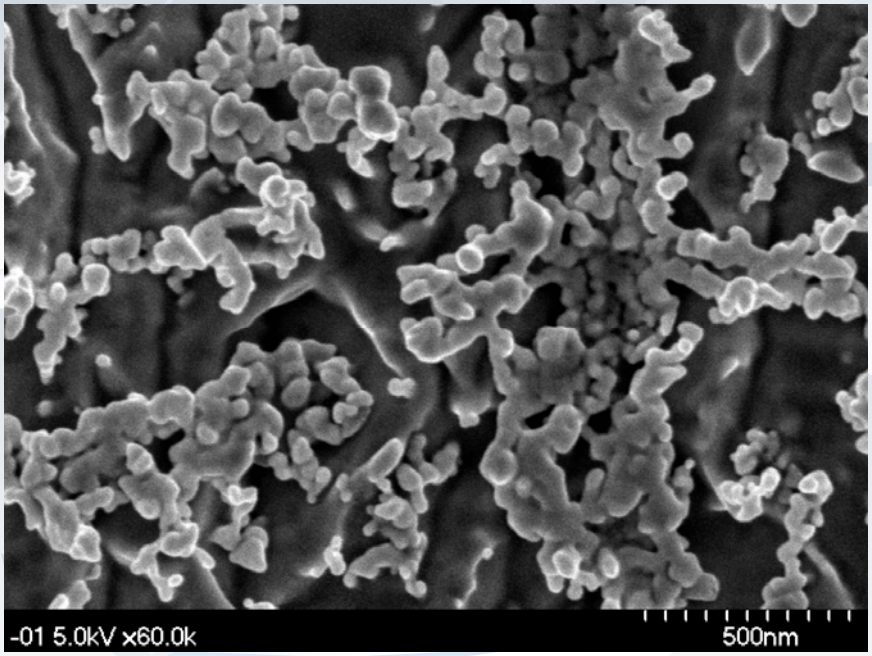


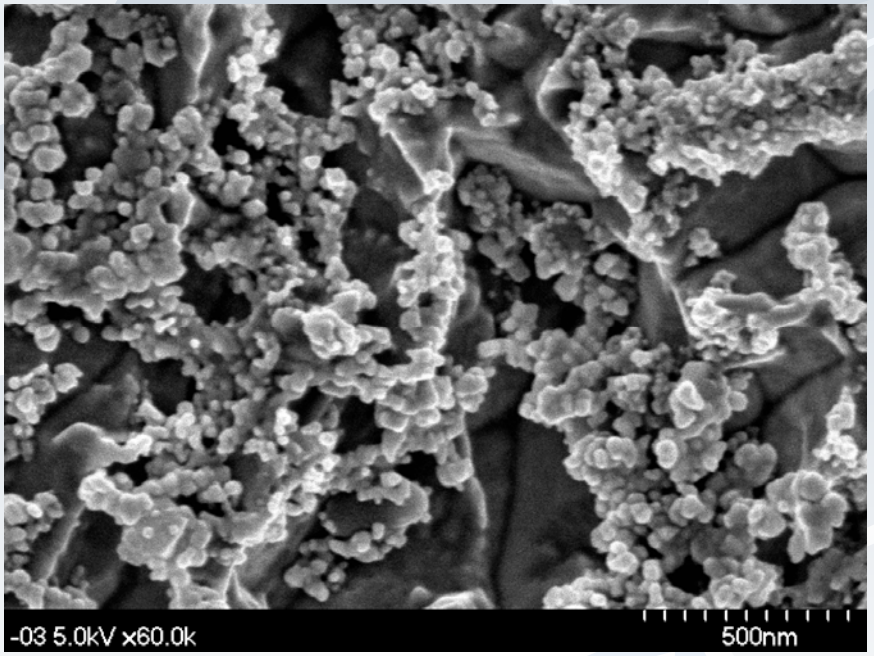


- Figure 24. Cyclic voltammograms at 500 mV/s of the 10th scan for electrochemically roughened gold substrates with predominant (220) orientation in different conditions. (a) In 0.1 M HCl. (b) In 1 mM TiO2 and 0.1 M HCl. (c) In 1 mM TiO2 and 0.1 M HCl, and irradiation with UV light of 4 W at 254 nm in the roughening procedure. The right figure displays the differentiable oxidation phenomenon occurring on the roughened gold substrates in the range of 0-0.65 V vs Ag/AgCl

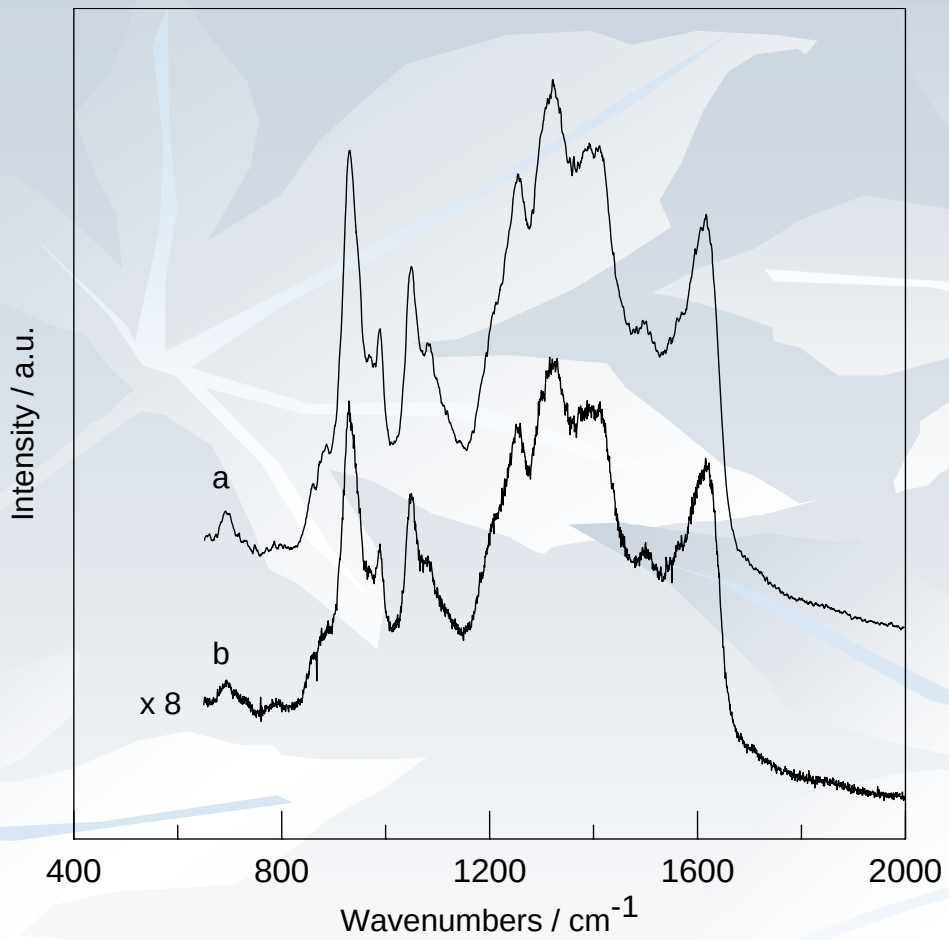


- Figure 25. SERS spectra of PPy electrodeposited on different substrates. (a) Electrochemically roughened gold modified with TiO2 nanoparticles and irradiation with UV light of 4 W at 254 nm in the roughening procedure. (b) Electrochemically roughened gold modified with TiO2 nanoparticles in the absence of UV light in the roughening procedure; the intensity was magnified by 4-fold. (c) Electrochemically roughened gold; the intensity was magnified by 5-fold.

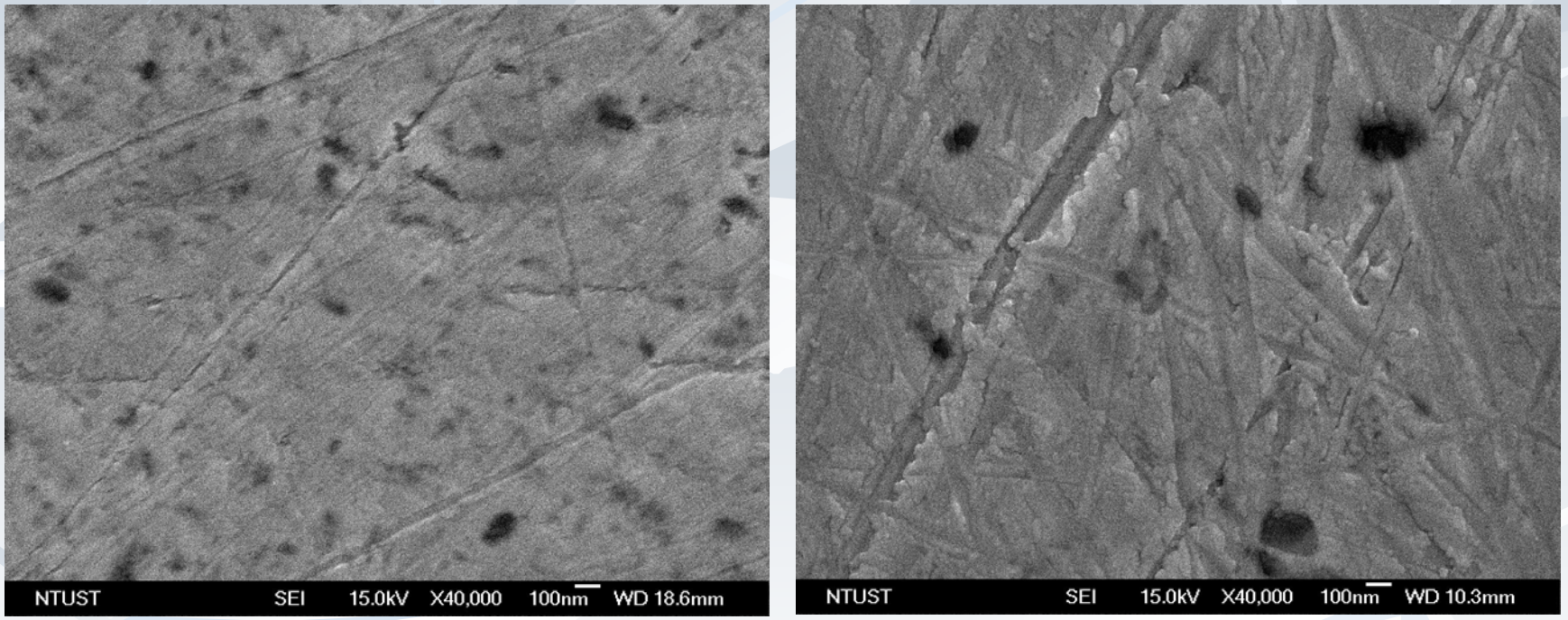




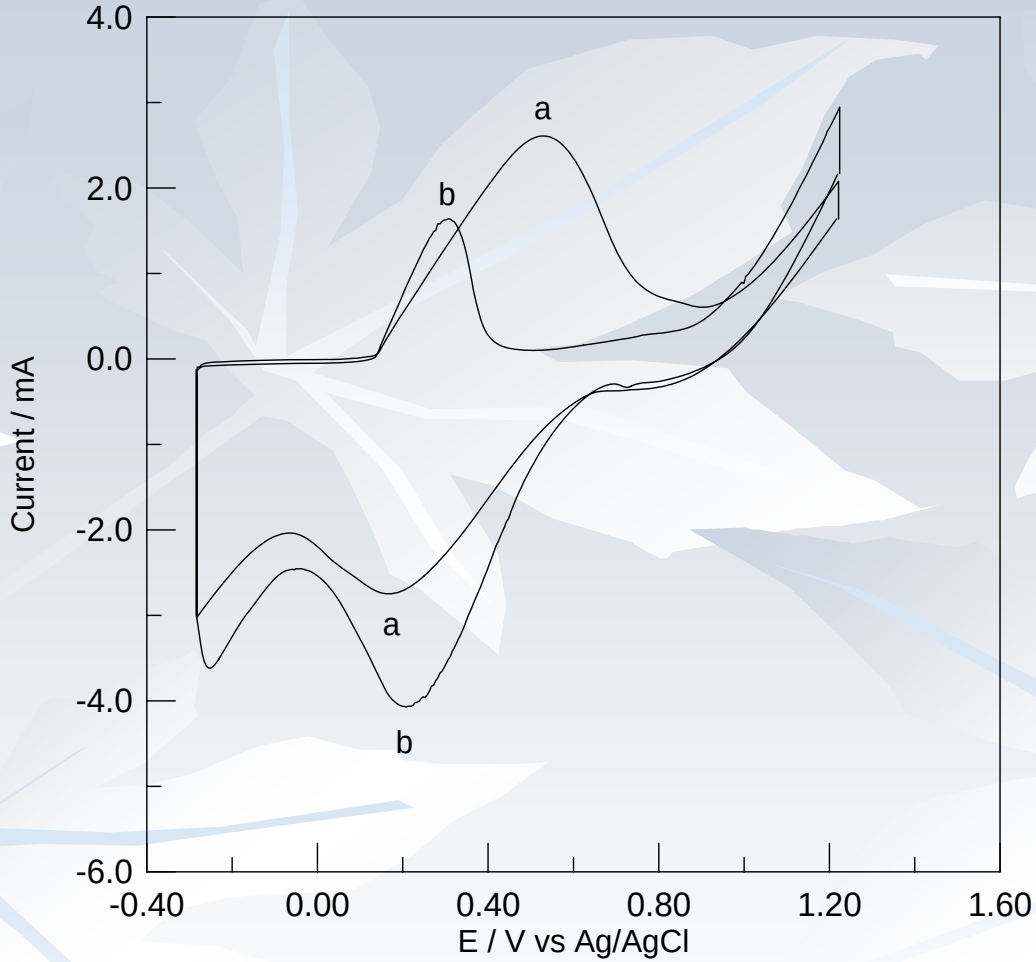
- Figure 31. SEM images of different substrates. (left) Electrochemically roughened gold. (right) Electrochemically roughened gold modified with silver nanoparticles.



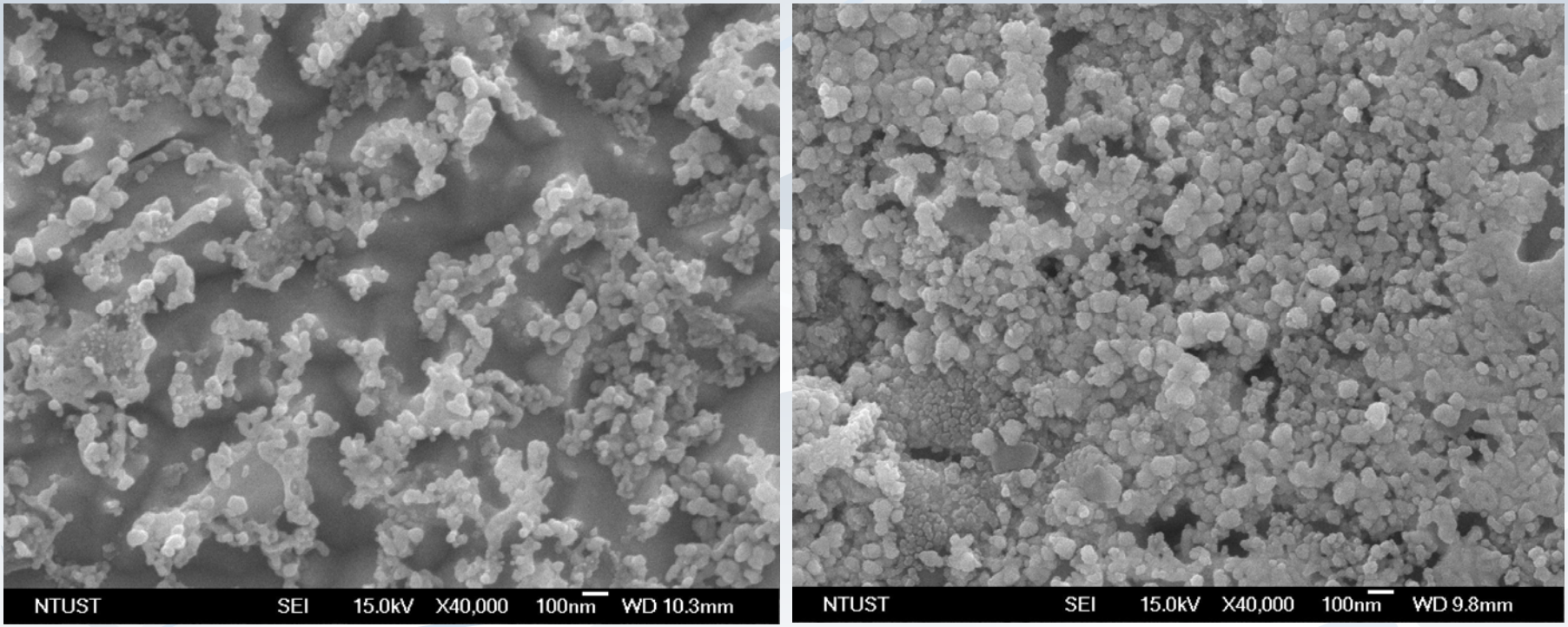
- Figure 27. SERS spectra of PPy electrodeposited on different substrates. (a) Electrochemically roughened gold modified with silver nanoparticles. (b) Electrochemically roughened gold; the intensity was magnified by 8-fold.



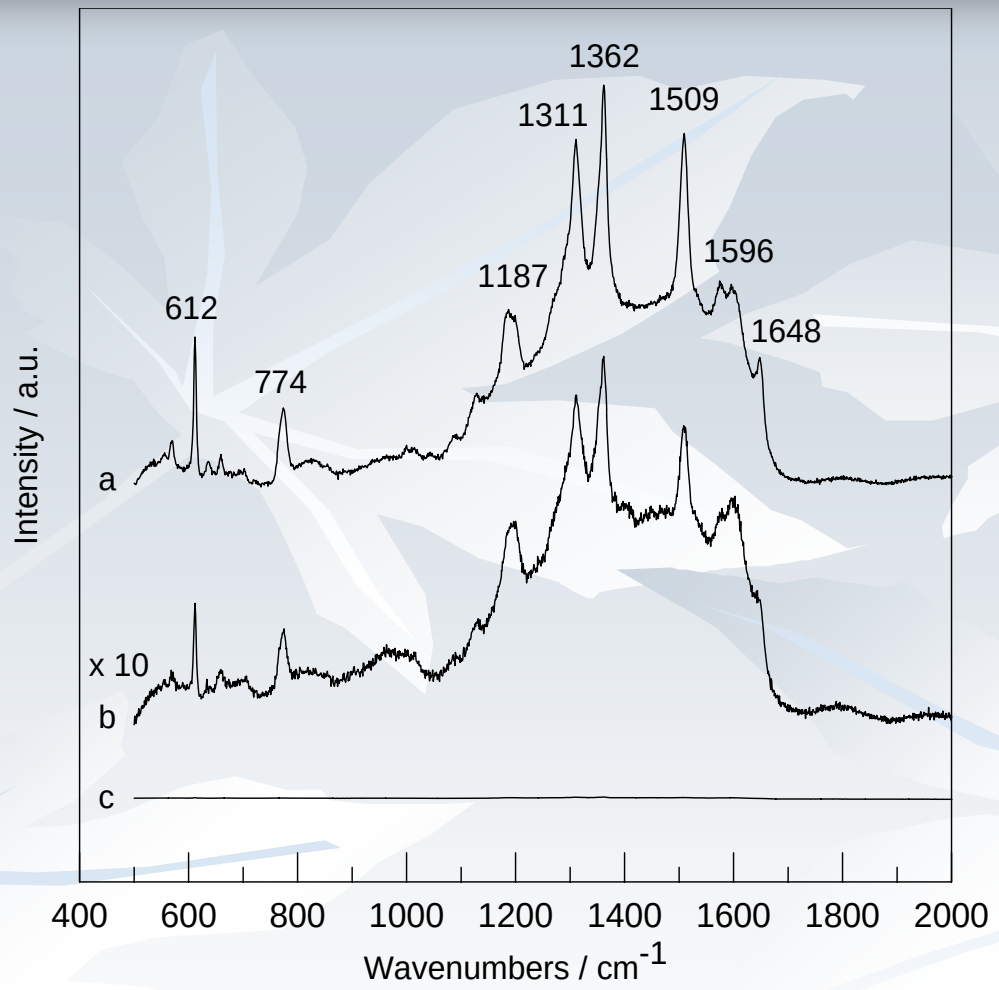
- Fig. 28. SEM images of different gold substrates. (left) Mechanically polished gold substrate. (right) Mechanically polished gold substrate modified by argon plasmas treatment.
- Basically, both the two substrates show similar and flat surface morphologies.



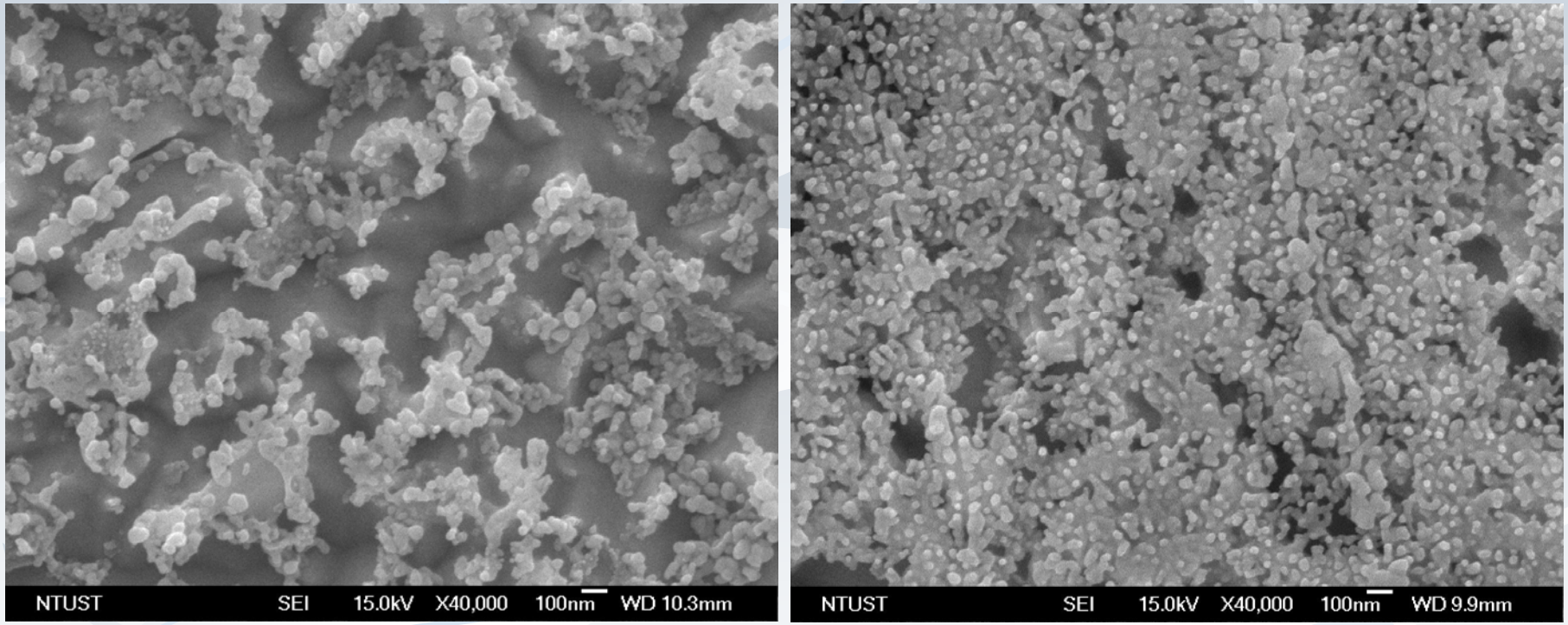
- Fig. 29. I-E curve for roughening gold substrates with (curve a) and without (curve b) the plasmas pretreatment.
- It is interesting that the plasmas treatment demonstrates a significant effect on the redox behavior of gold in CV.



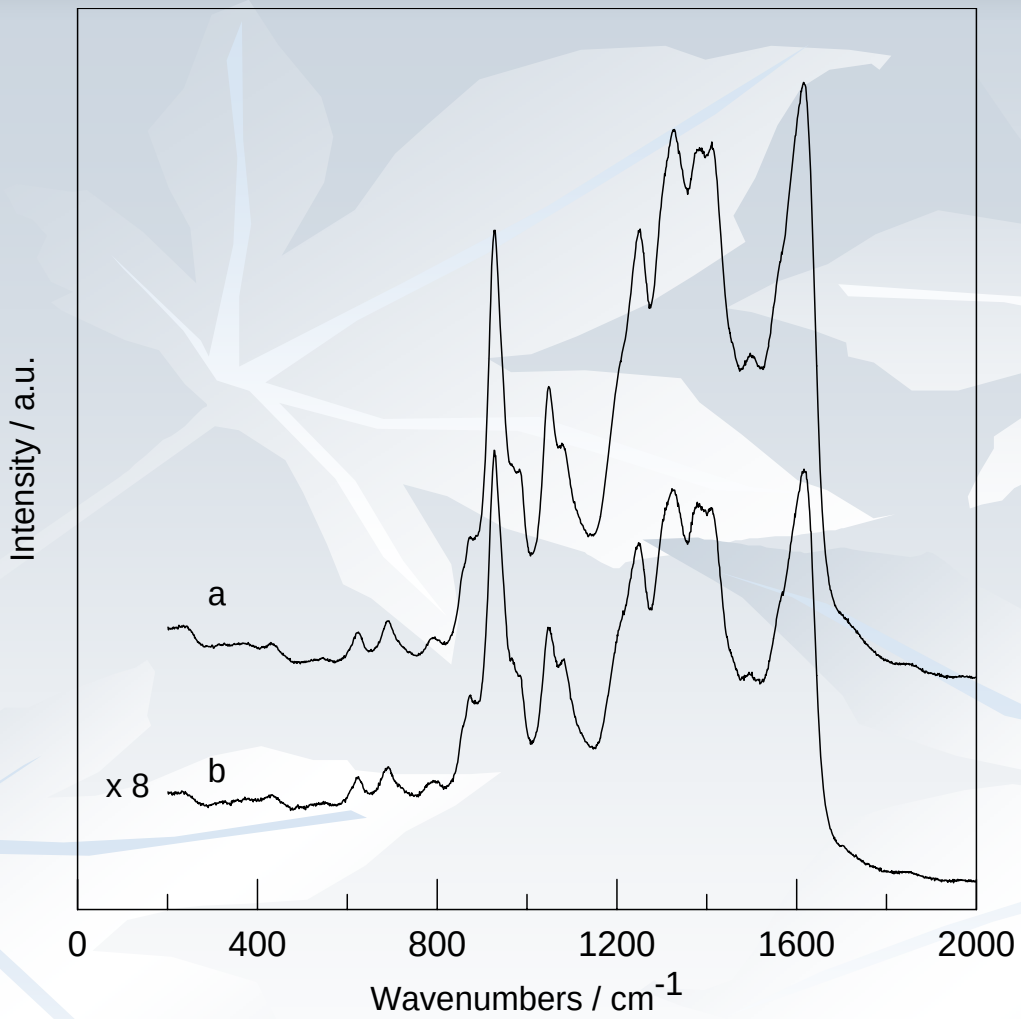
- Fig. 30. SEM images of different roughened gold substrates. (left) Electrochemically roughened gold substrate. (right) Electrochemically roughened gold substrate modified by argon plasmas pretreatment.
- With the plasmas pretreatment to the Au substrate, the surface morphology demonstrates an evener surface with close packing nanoparticles.



- Fig. 31. SERS spectra of R6G adsorbed on different gold substrates. (a) Electrochemically roughened gold substrate modified by argon plasmas pretreatment. (b) Electrochemically roughened gold substrate; the intensity was magnified by 10-fold. (c) Mechanically polished gold substrate.



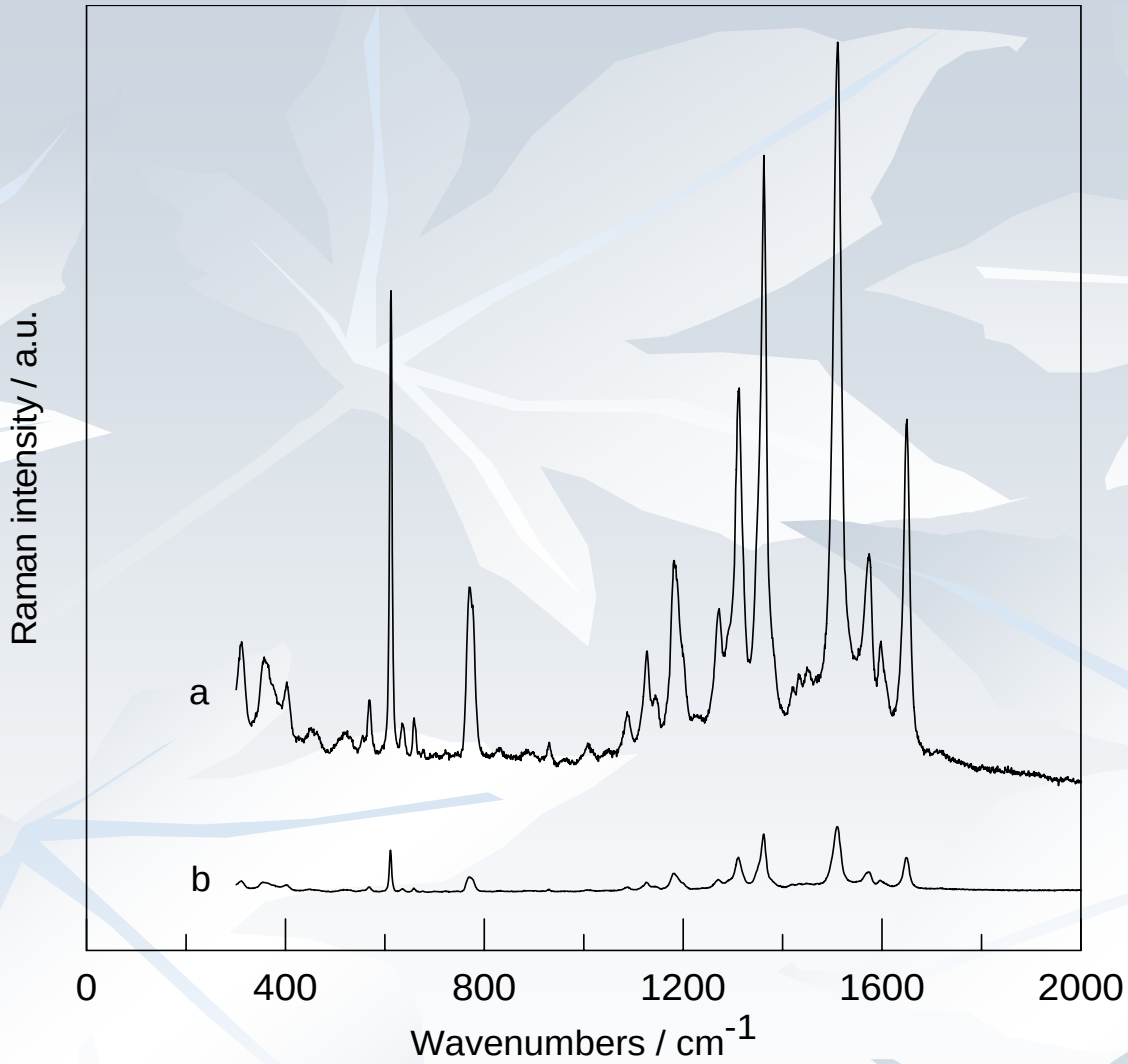
- Fig. 32. SEM images of different roughened gold substrates. (left) Electrochemically roughened gold substrate. (right) Electrochemically roughened gold substrate modified by argon plasmas post-treatment.
- With the plasmas post-treatment to the roughened Au substrate, the surface morphology of the modified roughened Au substrate becomes thicker and finer .



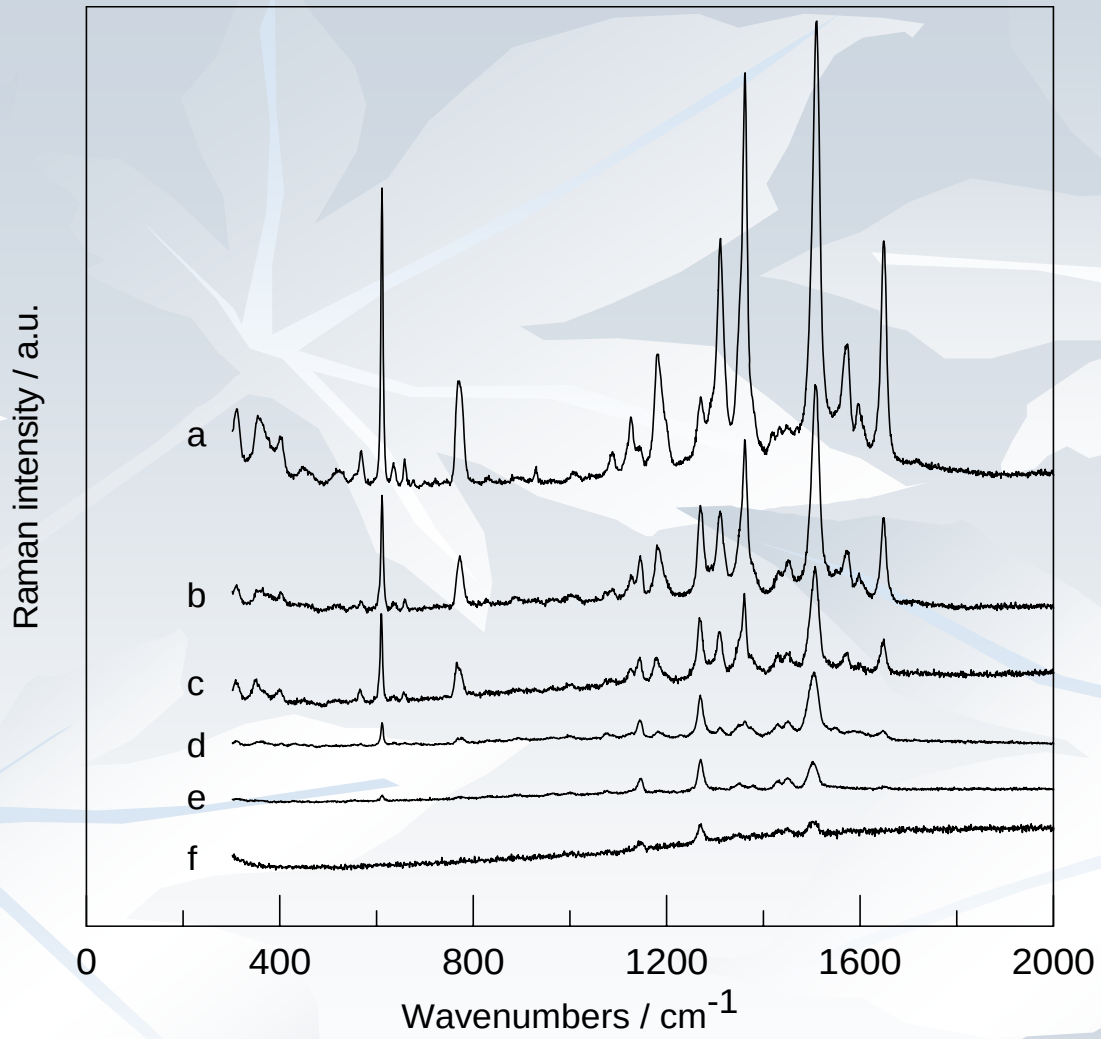
- Fig. 34. SERS spectra of PPy electrodeposited on different substrates. (a) Electrochemically roughened gold substrate modified by argon plasmas treatment. (b) Electrochemically roughened gold substrate; the intensity was magnified by 8-fold.

- Generally roughened Ag substrate ：electrode was cycled in 0.1 N KCl from -0.3 to +0.3 V vs Ag/AgCl at 5 mV/s for 3 scans

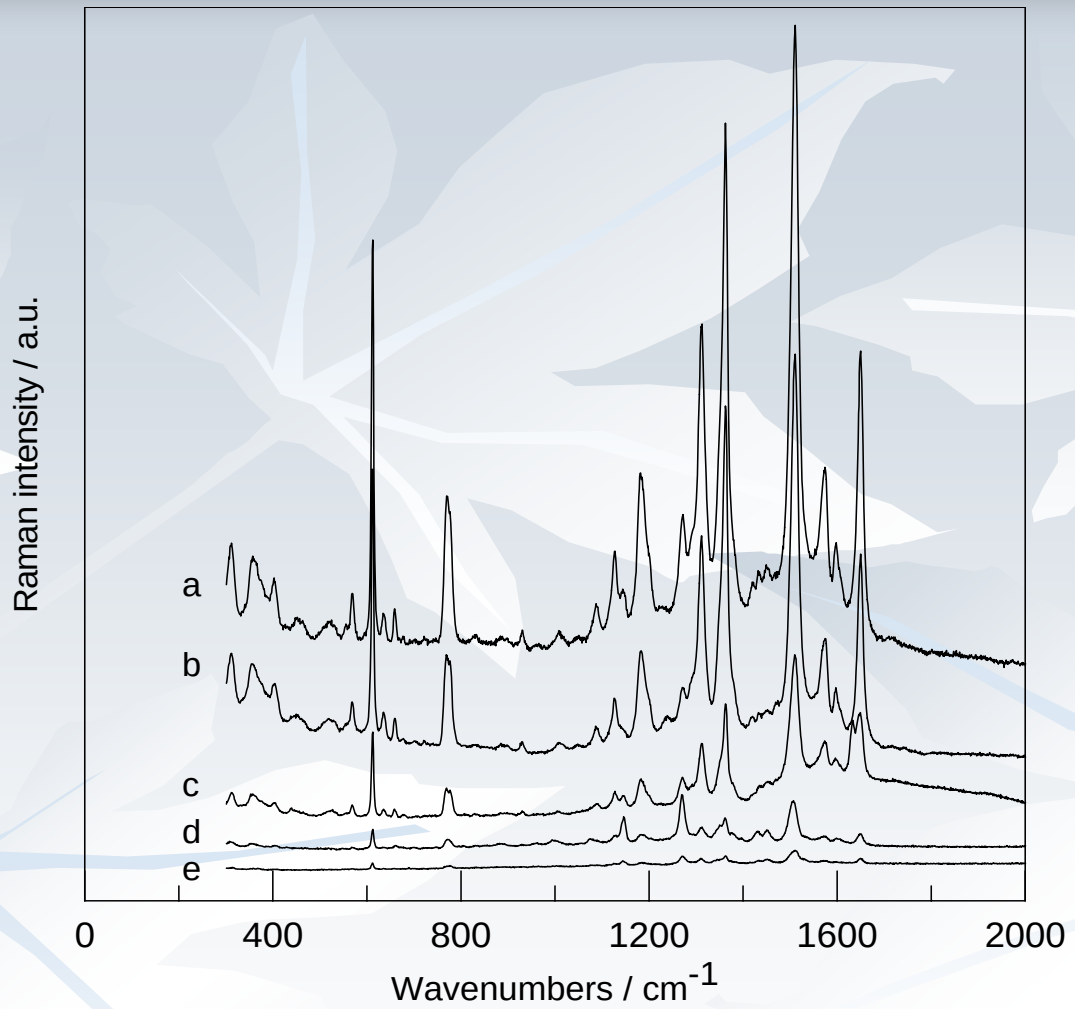
- Optimum procedure-prepared roughened Ag substrate ：electrode was cycled in 0.1 N NaCl from -0.3 to +0.2 V vs Ag/AgCl at 25 mV/s for 5 scans



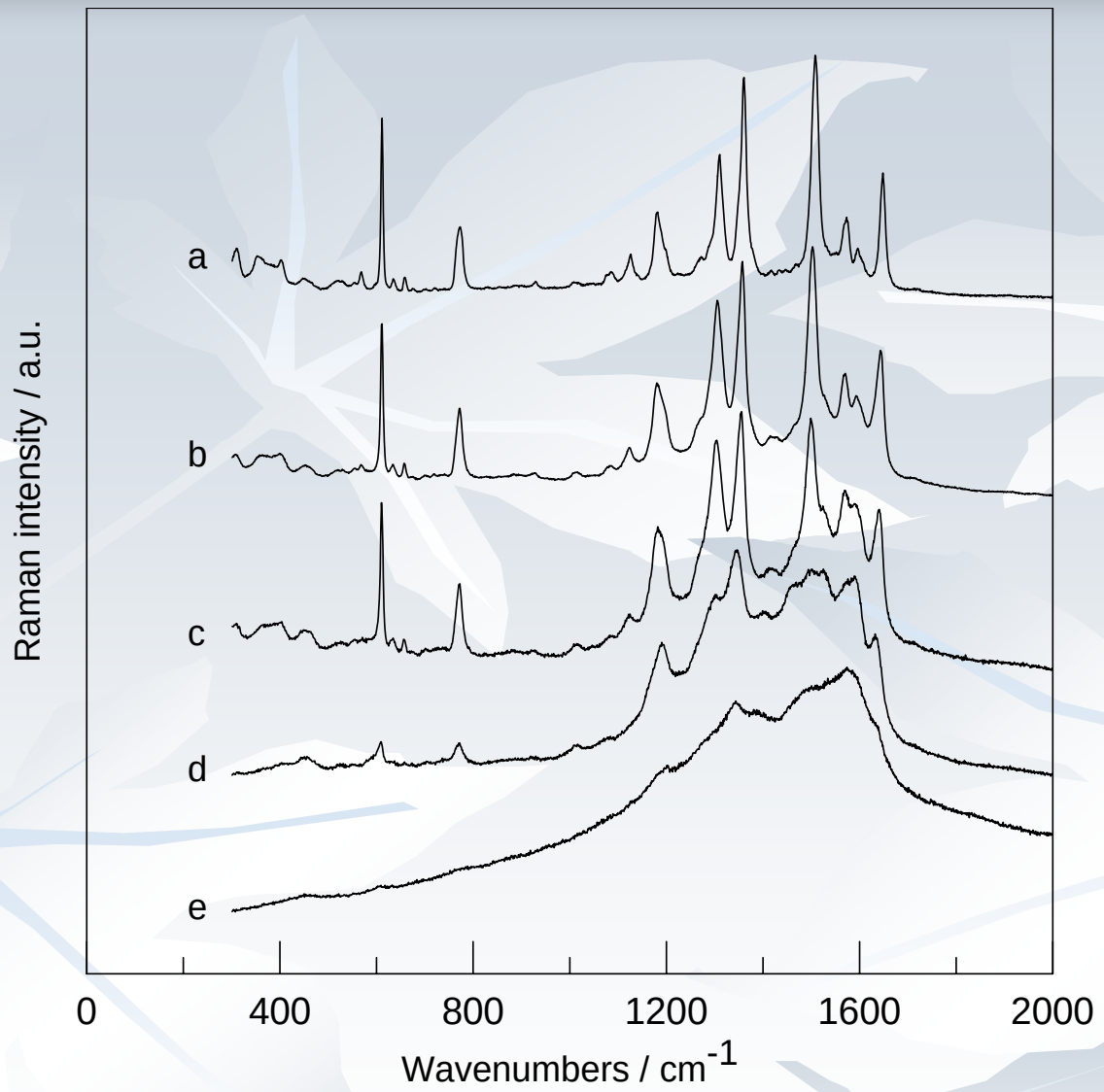
- Fig. 35. Spectra a and b representing R6G on the optimum procedure-prepared roughened Ag substrate and on the generally roughened Ag substrate, respectively.



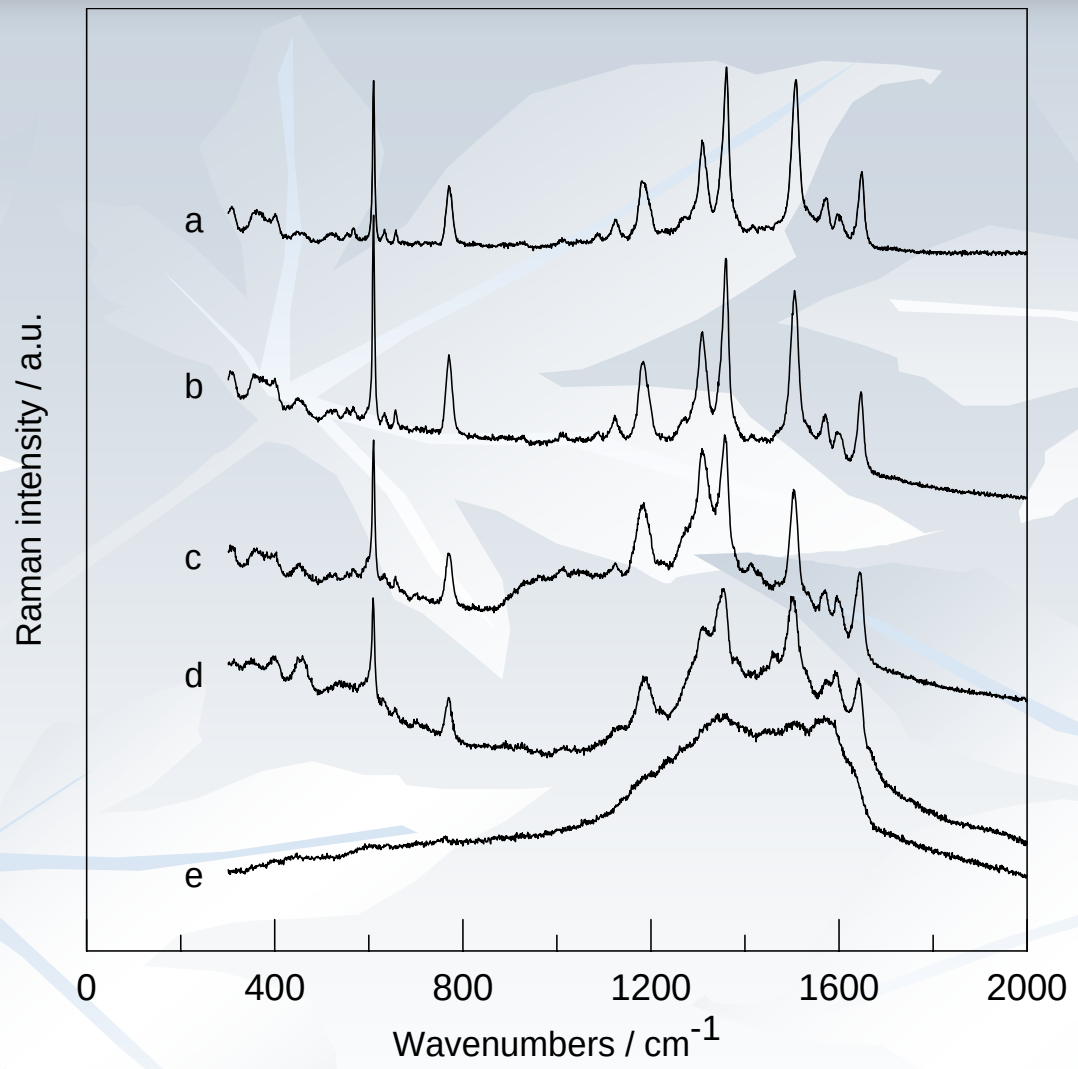
- Fig. 36. Spectra a~f representing different concentrations of 2×10^{-5}, 2×10^{-6}, 2×10^{-7}, 2×10^{-8}, 2×10^{-9} and 0 M, respectively, of R6G adsorbed on generally roughened Ag.



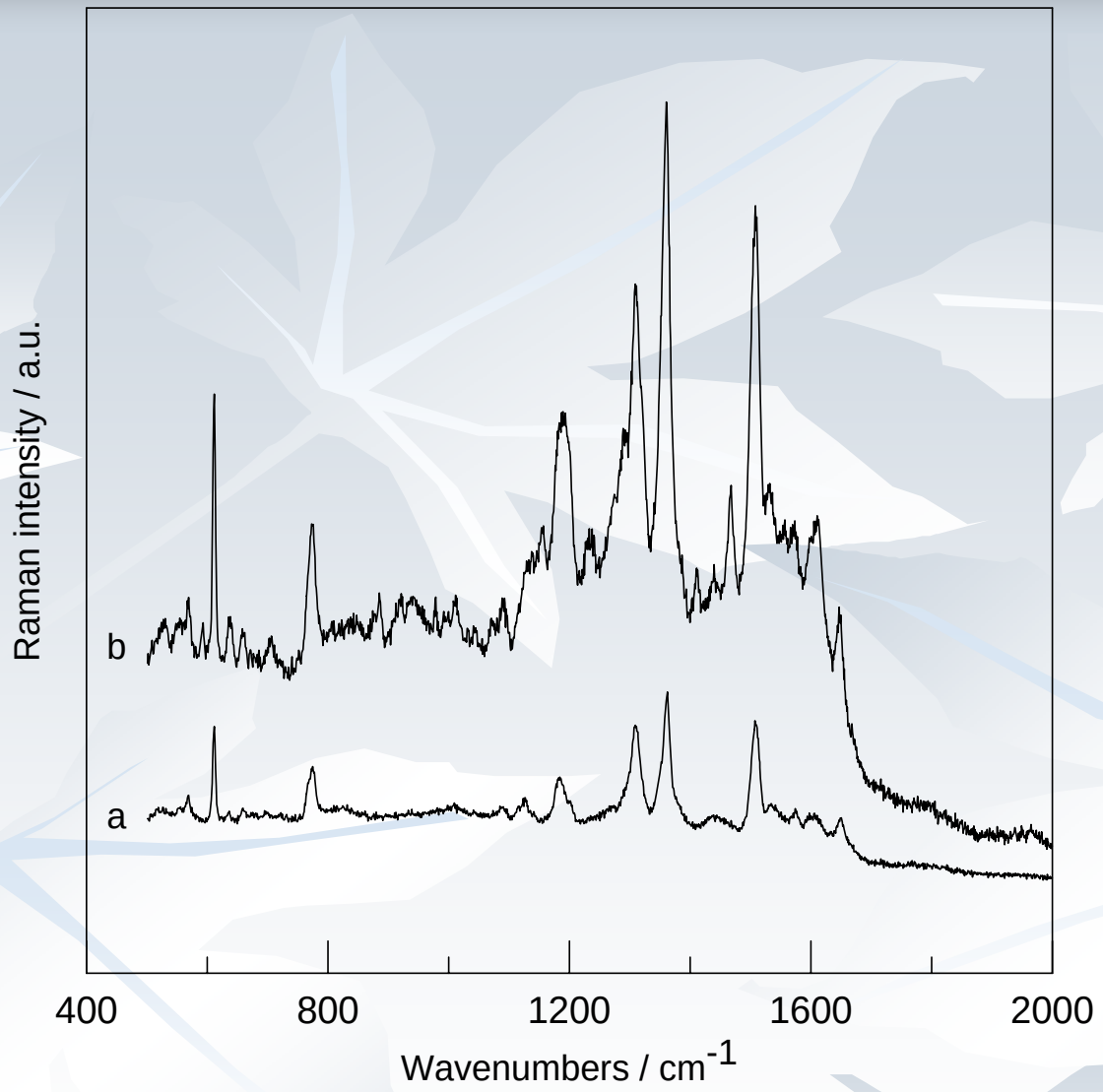
- Fig. 37. Spectra a~f representing different concentrations of 2×10^{-5}, 2×10^{-6}, 2×10^{-9}, 2×10^{-12}, 2×10^{-15} and 0 M, respectively, of R6G adsorbed on optimum procedure-prepared roughened Ag.



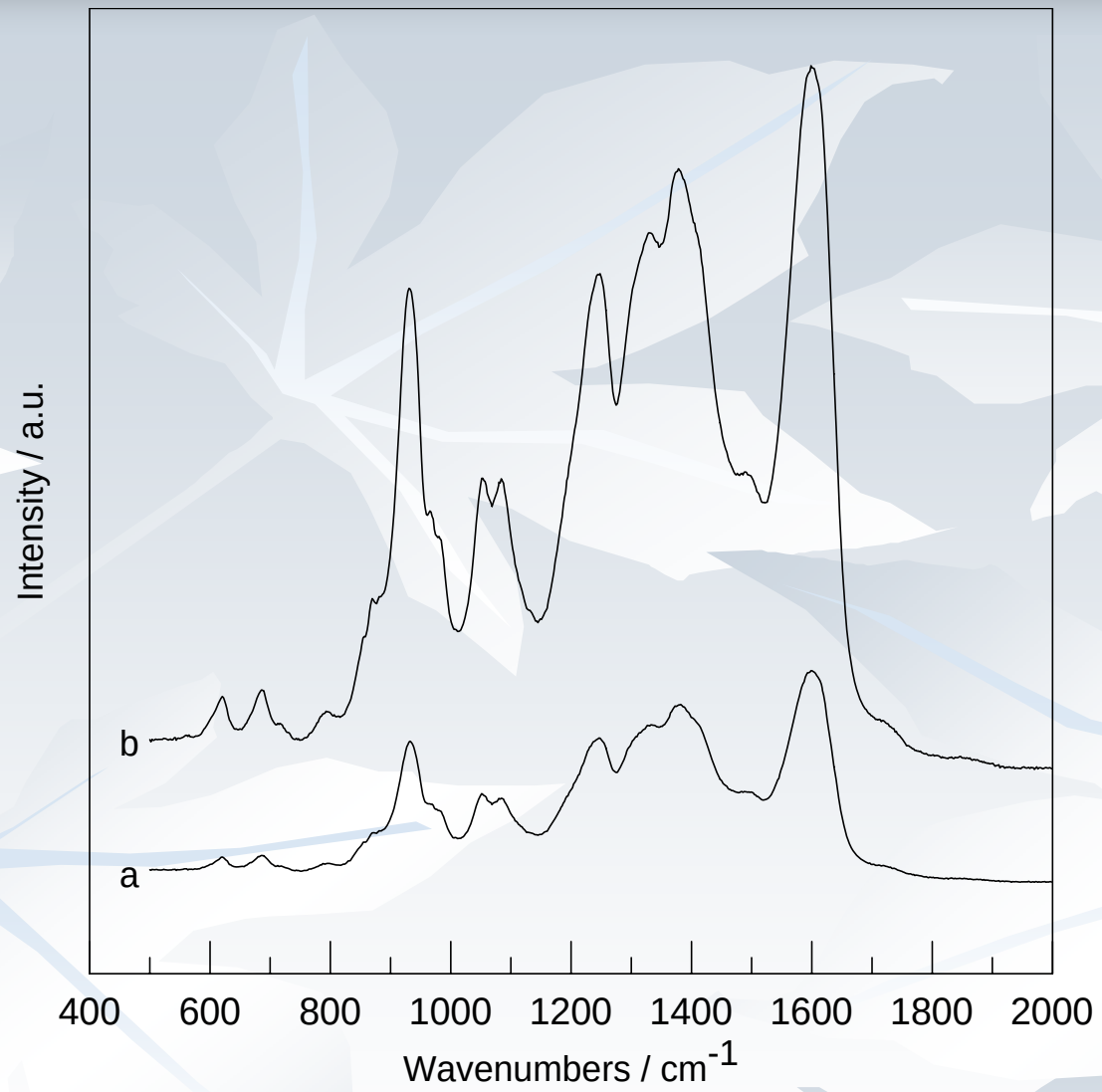
- Fig. 38. SERS spectra of R6G adsorbed on the roughened Au substrate treated at 25, 150, 200, 225 and 250 ^{o}C, respectively.



- Fig. 39. SERS spectra of R6G adsorbed on the roughened Ag substrate treated at 25, 75, 125, 150 and 250 ^{o}C, respectively.



- Fig. 40. SERS spectra of R6G adsorbed on the roughened Au substrate treated at 25 and 40 ^{o}C, respectively.



- Fig. 41. SERS spectra of PPy deposited on the roughened Au substrate treated at 25 and 35 ^{o}C, respectively.

Thank you for your attention