Surface plasmon resonance investigation of gold nanoparticle aggregation on self-assembled monolayers

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Motivation

pH sensor applications

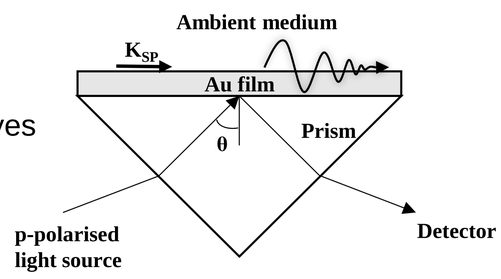
- **pH electrodes** [1] → Bulky size
- **Colorimetric pH sensors** [2] → Reversible
- **Optical pH sensors** [3] → Leaching of dyes

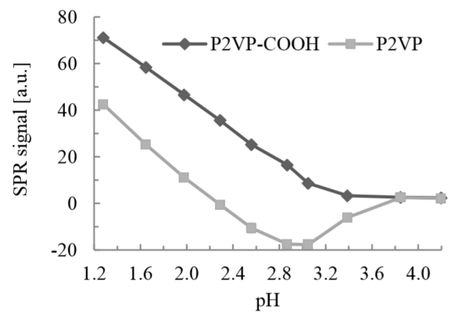
Surface plasmon resonance (SPR)

- Optical label free method
- Based on refractive index (RI) change

Fundamentals

SPR as an optical pH sensor [4, 5]

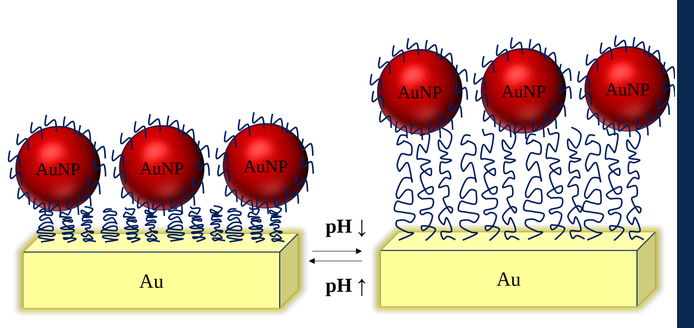




pH response of poly(2-vinylpyridine) (P2VP), and P2VP-COOH [4].

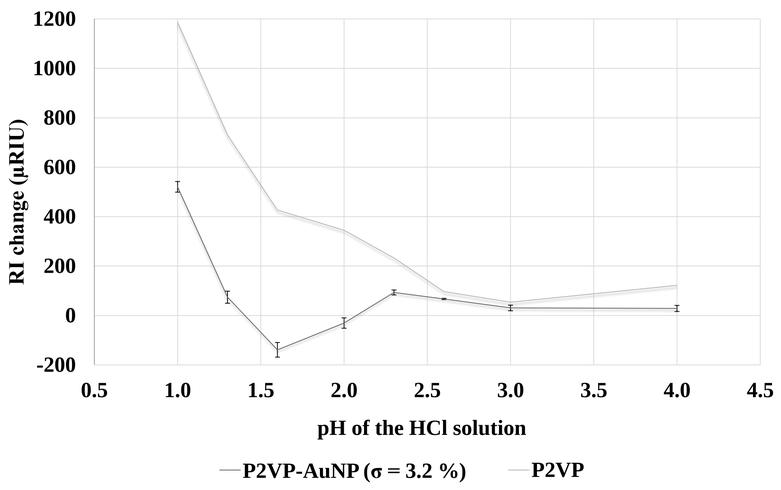
Idea

Signal enhancement of pH-sensitive polymers [5] **by AuNP**

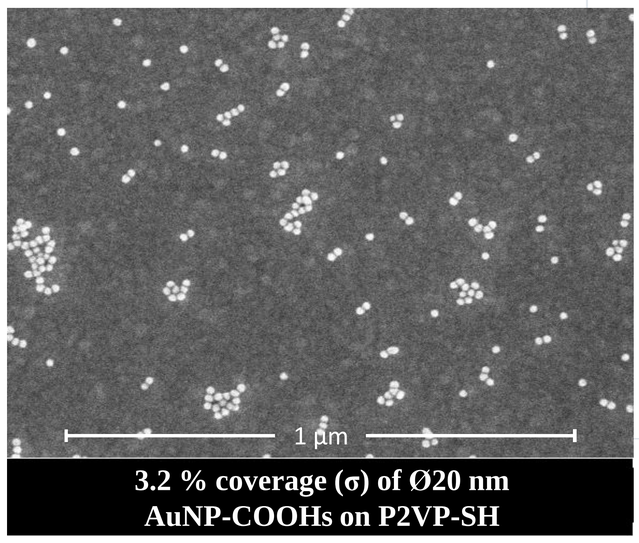


Results

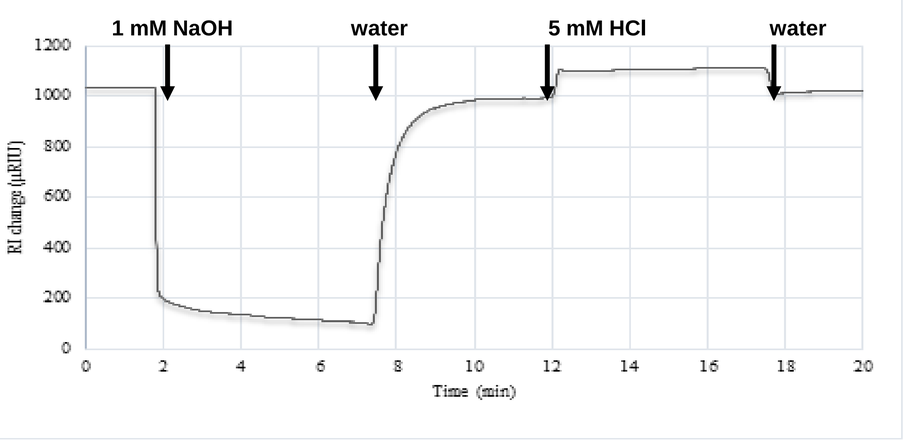
I) SPR sensor surface with P2VP-SH and AuNP-COOHs



pH response of P2VP-SH with (σ = 3.2 %) and without AuNP-COOHs. Enhanced decrease SPR signal due to swelling on the surface with AuNP-COOHs.



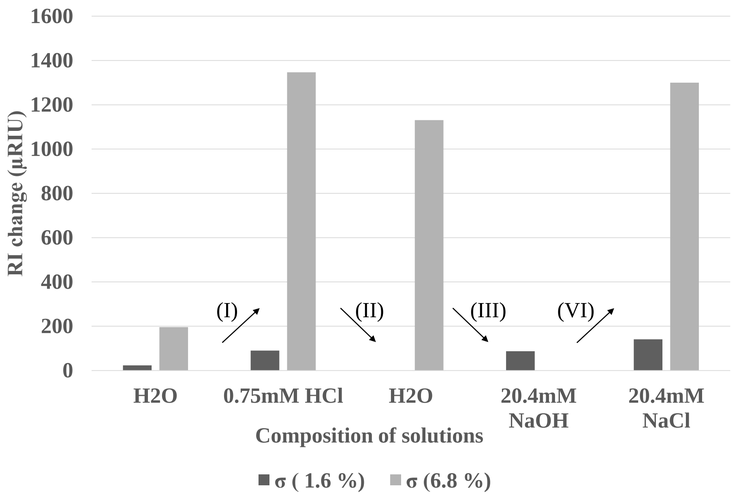
3.2 % coverage (σ) of Ø20 nm AuNP-COOHs on P2VP-SH



Kinetics of RI change on P2VP-SH SAM with AuNP-COOHs.

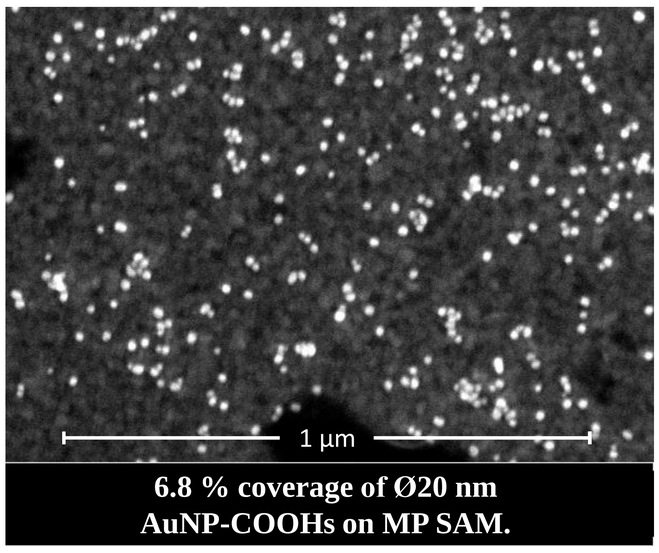
Highly sensitive towards high pH values, pH 11. AuNP-COOHs repulsion on the shrunk polymer result in a strong decrease in SPR signal.

II) SPR sensor surface with 4-mercaptopyridine (MP) (have no swelling effect) and AuNP-COOHs.

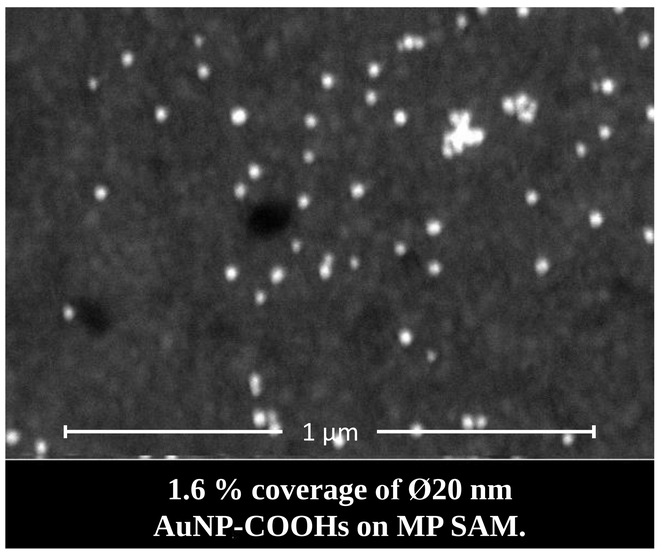


I) HCl solution
II) Water
III) NaOH solution
IV) Neutralising by HCl solution

Aggregation and disaggregation of AuNP-COOHs with different coverage.



6.8 % coverage of Ø20 nm AuNP-COOHs on MP SAM.

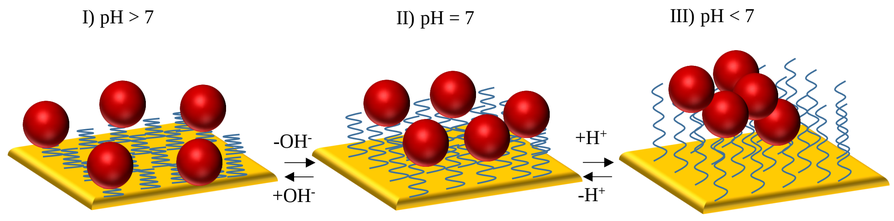


1.6 % coverage of Ø20 nm AuNP-COOHs on MP SAM.

Conclusion & Outlook

Conclusion

- **Swelling of polymers with AuNP-COOH at pH 2.3 to 1.7 (decrease in SPR signal)**
- **Distance increase between AuNPs and Au substrate (weaker Localised SPR coupling)**
- **Shrinking of polymers at pH 11 and AuNP-COOH disaggregation**
- **Strong decrease in SPR signal due to AuNP-COOH repulsion**



I. **Electrostatic repulsion of AuNP-COOHs accompanied by shrinkage of the P2VP chains at pH > 7.**
II. **At pH = 7, the P2VP chains are partly swollen and the AuNPs can approach each other.**
III. **Aggregation of the AuNP-COOHs accompanied by the complete swelling of P2VP chains at pH < 7.**

Outlook

- **Different AuNP size, shape (octahedral, rod, triangle) and with other functionalities ($-NH_2$)**
- **Different pH-sensitive polymers with acidic functional group (-COOH)**
- **Microfluidic sensor system**

References

1. E. Bakker and A. Xu, E. Pretsch. Optimum composition of neutral carrier based pH electrodes. Analytica Chimica Acta, 1994, 295, 253-262.
2. F. Qu, N. Bing Li, and H. Q. Luo. Highly Sensitive Fluorescent and Colorimetric pH Sensor Based on Polyethylenimine-Capped Silver Nanoclusters. Langmuir. 2013, 29, 1199-1205.
3. Z. Jin, Y. Su, and Y. Duan. An improved optical pH sensor based on polyaniline. Sensors and Actuators B, 2000, 71, 118-122.
4. Kick and M. Mertig. Characterization of pH-sensitive polymer layers by surface plasmon resonance and quartz crystal microbalance. Phys. Status Solidi A, (2015), DOI 10.1002/pssa.201431604.
5. I. Tokareva, S. Minko, J. H. Fendler, and E. Hutter. Nanosensors Based on Responsive Polymer Brushes and Gold Nanoparticle Enhanced Transmission Surface Plasmon Resonance Spectroscopy. J. AM. CHEM. SOC. 2004,126, 15950-15951.

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