

Metallic Atom-Scale Junction for Chemical Noise Detection: Study of Surface Molecular Adsorption/Desorption Kinetics using Fluctuation Spectroscopy

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Metallic atom-scale junctions (ASJs) have great potential as chemical sensors because chemical adsorption of Lewis bases causes an enormous conductance change compared to thin film or nanowire sensors.¹ The mesoscopic structure of ASJs limits the number of adsorbing molecules, and because few molecules lead to a significant sensing signal, each adsorbate molecule gives a great contribution to the conductance signal. This suggests that the signal changes induced by surface population fluctuation at post-adsorption equilibrium, i.e. chemical noise, should be detectable by using metallic ASJs. The biggest motivation of detecting chemical noise is to reveal the important information about kinetics buried underneath the fluctuating signals.

Recently, we have reported a novel fabrication method to produce robust bimetallic Au-Ag-Au ASJs by generating directional galvanic Ag deposition between two nanogap electrodes in Ag_2SO_4 solution. Initially an overgrown junction is obtained, followed by a self-thinning process controlled by the chemical potential of the Ag^+ solution.² In order to create an ASJ that can survive solution switching, a slight modification is made. After the overgrown junction is formed, analyte, in our study, pyridine solution is delivered to the junction before self-thinning takes place. The thinning process is executed by manipulating current-induced electro-migration. The resulting ASJs can be stable in pyridine solution for very long (>1000 s) periods.

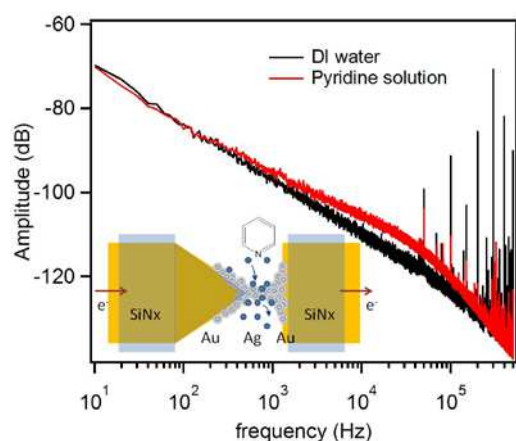


Figure 1. Power spectral density showing excess Lorentzian noise when measuring Ag ASJs in pyridine solution.

Chemical noise of pyridine adsorption/desorption can be observed and distinguished by applying sequential autocorrelation and Fourier transform to the time domain electrical signal to yield the power spectral density (PSD). $1/f$ background noise, originating from resistance fluctuations of ASJs, dominates at low frequencies, but an excess noise component occurs when pyridine is in solution. The excess noise has a Lorentzian distribution which is due to the adsorbed pyridine population fluctuation. The characteristic cutoff frequency, f_c ,

resulting from the relaxation time of the fluctuations contains information about adsorbate adsorption-desorption kinetics. Various experiments including kinetics-concentration dependency, response of f_c at different size ASJs, and comparison of different pyridine derivatives are done for pyridine-Ag ASJ system to characterize the excess chemical noise.

An interesting future direction for this work will explore how the chemical noise responds when the electrochemical potential of ASJs is controlled.

References

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