

# The Role of Cathode's Surface Properties in the Electrochemical Deuterium Loading of Pd Foils

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# INTRODUCTION

## Experimental Results

correlation between excess heat and cathode surface properties

- Morphology (PSD), crystal orientation, impurities

## Theoretical hints

Theoretical frames suggest electro-dynamical effects (plasmons excitation) to be involved in excess heat production

Local em field in-homogeneities affect electrochemical kinetics and metal/electrolyte interface reconstruction

# OUTLINE

## Role of surface in PdH electrodynamics

### ➤ em field enhancement (plasmon excitation)

- Morphology

- Dielectric constant



E. Castagna S10\_O4

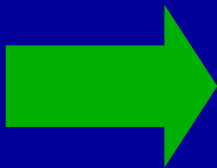
### ➤ Effects on Electro-chemical kinetics

interplay between kinetic parameters and surface morphology

# Role of surface morphology in electric field enhancement

*the em field can be enhanced close to a metal-dielectric interface via the excitation of surface plasmons (SP, collective oscillation modes of the free electrons)*

Surface roughness and isolated features make it possible the coupling of the em. field source with the SP modes, because **they provide additional wavevector** to the source em field to fulfill the required momentum conservation



***It is the wave-vector "content" of the surface morphology (i.e. the Power Spectrum) that play the role in the SP interaction.***

# Theoretical Approach to EM Field Enhancement Calculations

The rigorous calculation of the electric field enhancement produced by a *real* surface profile is a very complicated task, that needs a model for the surface profile.

Some particular ideal cases have been studied, from which physical insight can be extracted:

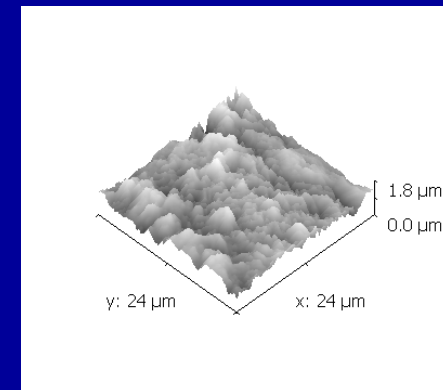
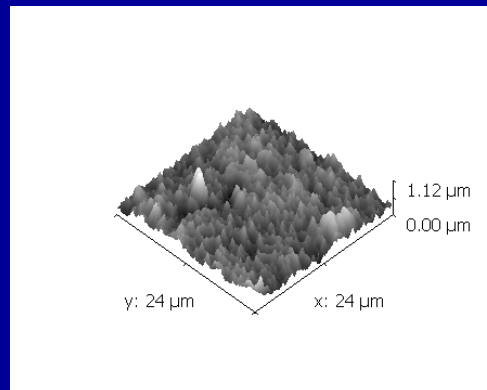
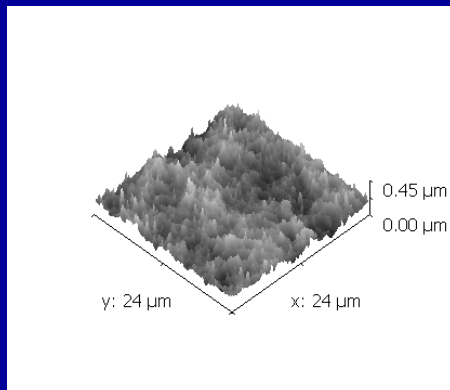
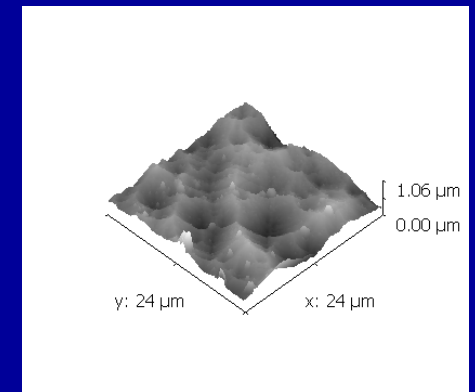
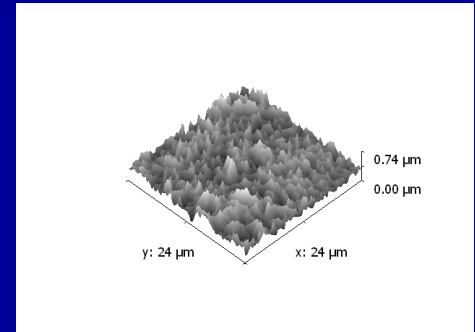
- 1) periodic gratings
- 2) moderately rough random surface profiles
- 3) isolated sub-wavelength particles
- 4) completely disordered patterns (Anderson-like)
- 5) fractal percolating aggregates

# What does our sample surface look like more?

Not –engineered Pd foils, prepared by cold rolling, thermal annealing, acid etching and undergone to electrochemical D (H) loading

Microscopy images (AFM,SEM):

➔ **moderately rough random surfaces**



# Theory <sup>[1]</sup> :

- the surface profile  $\zeta(x,y)$  is described as the **superposition** of several **sinusoidal diffraction gratings**:

$$z = \zeta(x, y) = \sum_{\vec{G}} \zeta_G e^{i\vec{G} \cdot \vec{R}}$$

where  $R$  is the spatial coordinate  $(x,y)$  and the  $\langle \zeta(x,y) \rangle = 0$

- to **first order theory in  $\zeta/\lambda$** , the scattering of an em wave from the surface  $\zeta(x,y)$  is reduced to the superposition of the scatterings from single sinusoidal diffraction gratings, each characterized by an amplitude  $\zeta_G$

- SP excitation by light in a sinusoidal grating with wave-vector  $\mathbf{G}$  is allowed if the following matching conditions are satisfied:

$$\mathbf{G} = \mathbf{K}_{sp} - \mathbf{K}_{inc} \quad (1)$$

$$\mathbf{K}_{sp} = (2\pi/\lambda)^2 \text{Real}(\epsilon_m / (\epsilon_m + \epsilon_d)) \quad (2)$$

where  $\mathbf{K}_{inc}$  is the projection of the incident wave-vector into the XY plane,  $\epsilon_m$  is the metal dielectric constant and  $\epsilon_d$  is the dielectric constant of the adjacent medium

[1] A. Marvin, F. Toigo, V. Celli, Phys. Rev. B 11, 2777 (1975)

# SP excitation probability

It results that the SP excitation probability ( $\Delta R_{sp}$ )

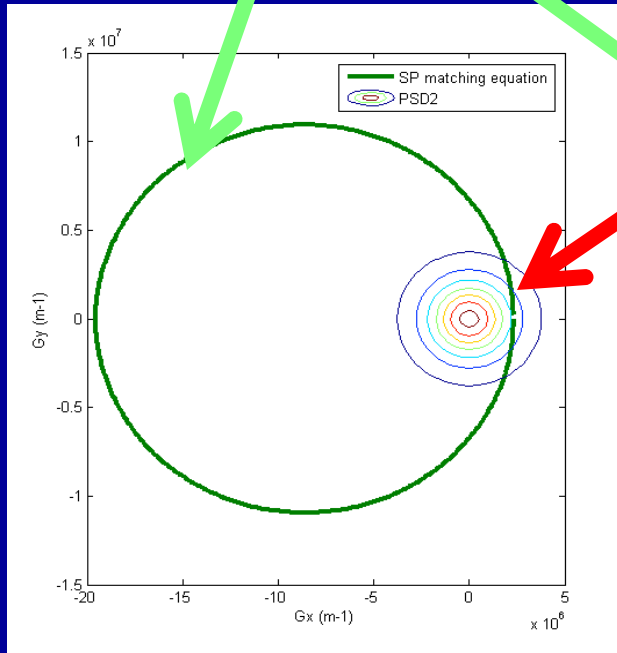
$$\Delta R_{sp} = (2\pi/\lambda)^4 \cos(\theta_{inc}) \int \text{PSD}(\mathbf{G}) \text{factor}(\mathbf{G}, \theta_{inc}, \varepsilon_m, \varepsilon_d) \delta(|\mathbf{G}|^2 - |\mathbf{K}_{sp} - \mathbf{K}_{inc}|^2) d\mathbf{G} \quad (3)$$

- $\theta_{inc}$  and  $\lambda$  are the incident angle and wavelength;
- $\text{factor1}(\mathbf{G}, \theta_{inc}, \varepsilon_m, \varepsilon_d)$  is a factor that does not depend on the surface profile;
- the integral is on domain made of wave-vectors  $\mathbf{G}$  matching the SP excitation condition;
- the **Power Spectral Density** (PSD) of the surface is defined as  $\text{PSD}(\mathbf{G}) = (L/2\pi)^2 |\zeta_{\mathbf{G}}|^2$

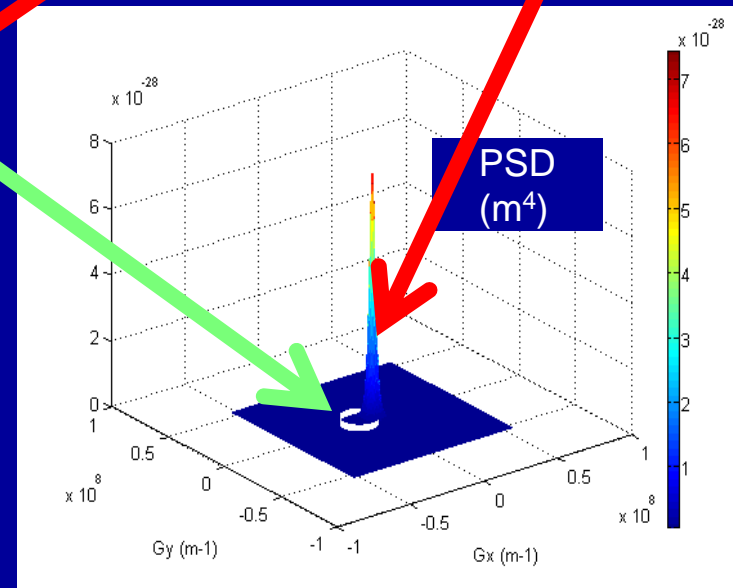
From the knowledge of  $\text{PSD}(\mathbf{G})$  at the wave-vectors  $\mathbf{G}$  matching (1) and (2) it is possible to find  $\Delta R_{sp}$  from (3)



# Wave-vector domain matching the SP excitation condition (eq. 1)



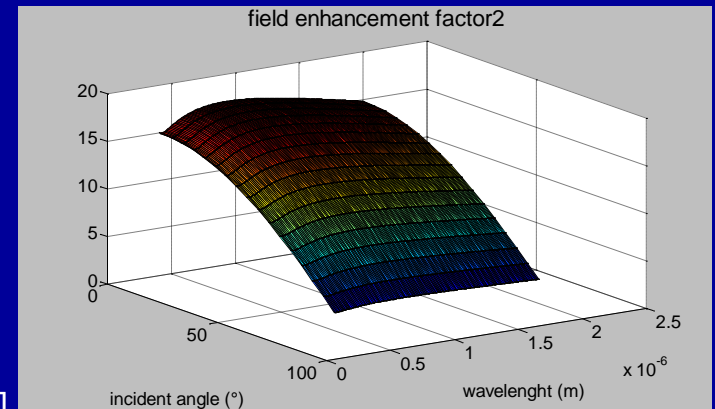
# Power Spectral Density



Surface profiles with higher values of the PSD at the wave-vector  $\mathbf{G}$  indicated by the circle have higher probability to support Surface -Plasmon modes.

# SP Electric Field Enhancement

The Electric field associated to the SP charge oscillation is enhanced because of its spatial confinement close to the interface.



The enhancement ratio ( $|E_{sp}|^2/|E_{inc}|^2$ ) is given by [2]

$$|E_{sp}|^2/|E_{inc}|^2 = \cos(\theta_{inc}) \text{factor2}(\lambda, \varepsilon_m, \varepsilon_d) \Delta R_{sp} \quad (4)$$

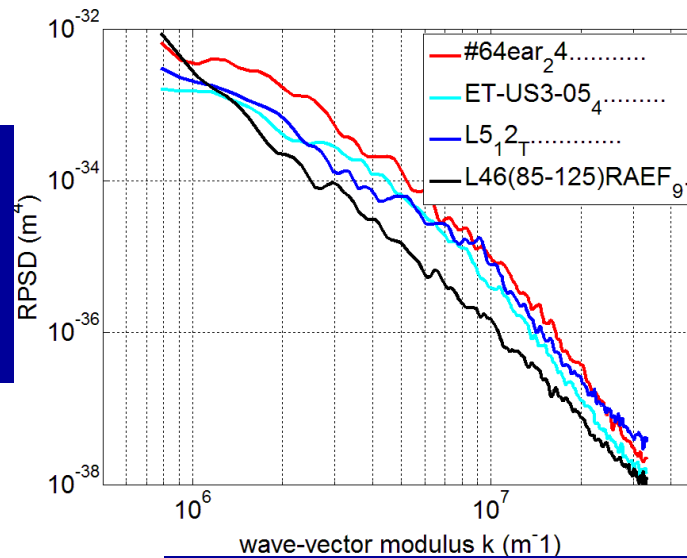
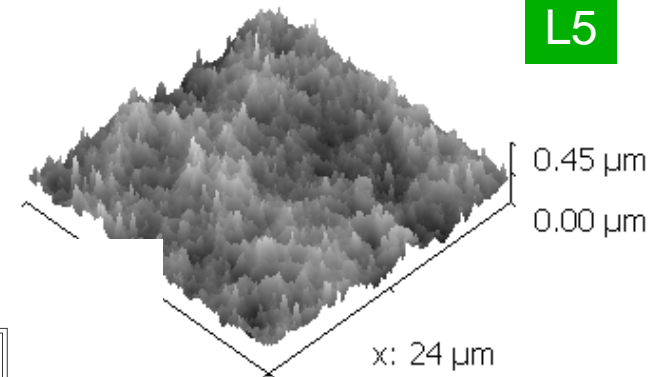
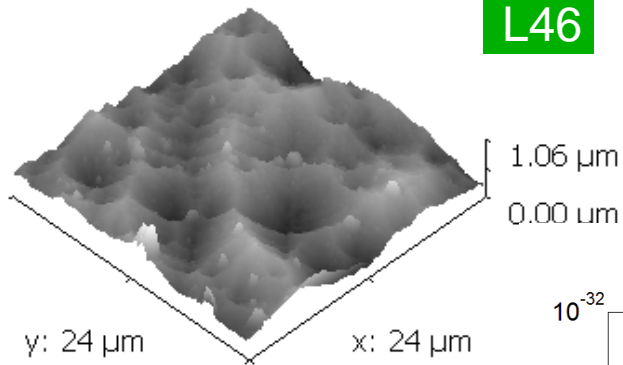
- $\theta_{inc}$  and  $\lambda$  are the incident angle and wavelength;
- $\text{factor2}(\lambda, \varepsilon_m, \varepsilon_d)$  is a factor that does depend only on the dielectric constants;
- $\Delta R_{sp}$  is the SP excitation probability defined in the previous slide

the **Power Spectral Density is obtained by the AFM images**

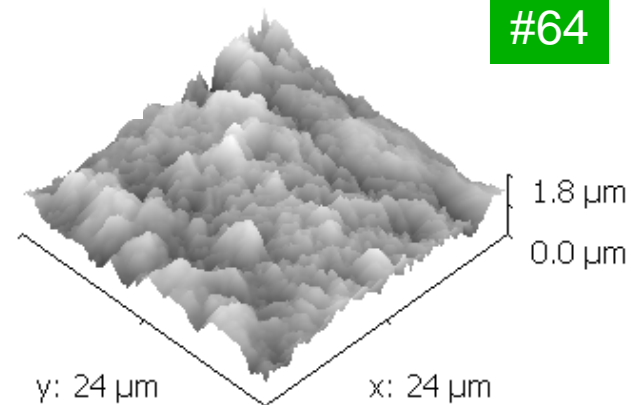
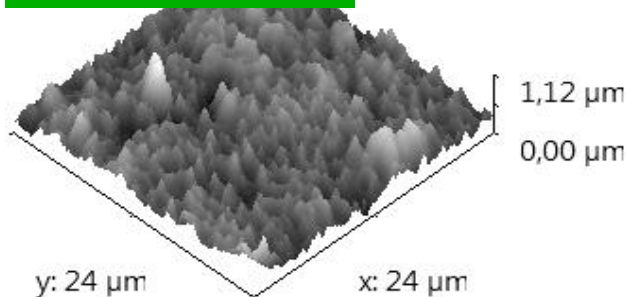
From the knowledge of PSD(**G**) at the wave-vectors **G** matching (1) and (2) it is possible to find  $\Delta R_{sp}$  from (3) and then  $|E_{sp}|^2/|E_{inc}|^2$  from (4)

[2] W. H. Weber, G. W. Ford, Optics Lett. 6, 122 (1981)

# Excess Heat Samples after electrolysis

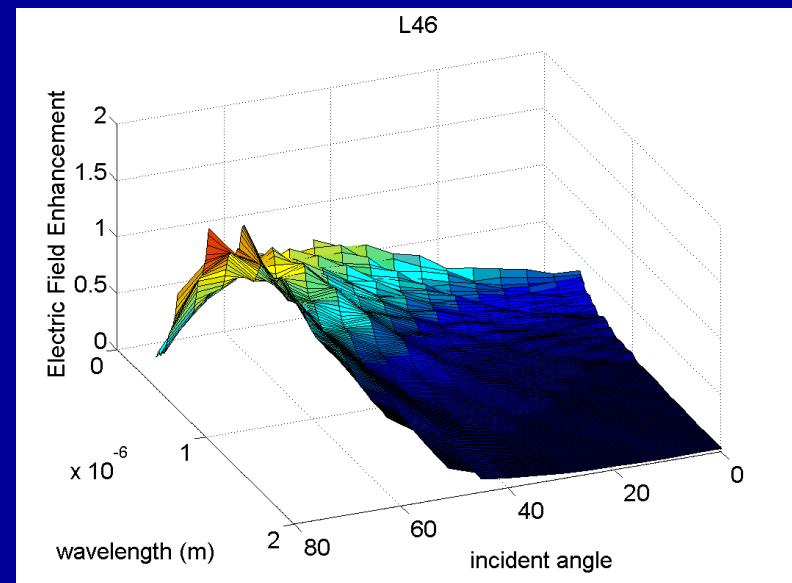
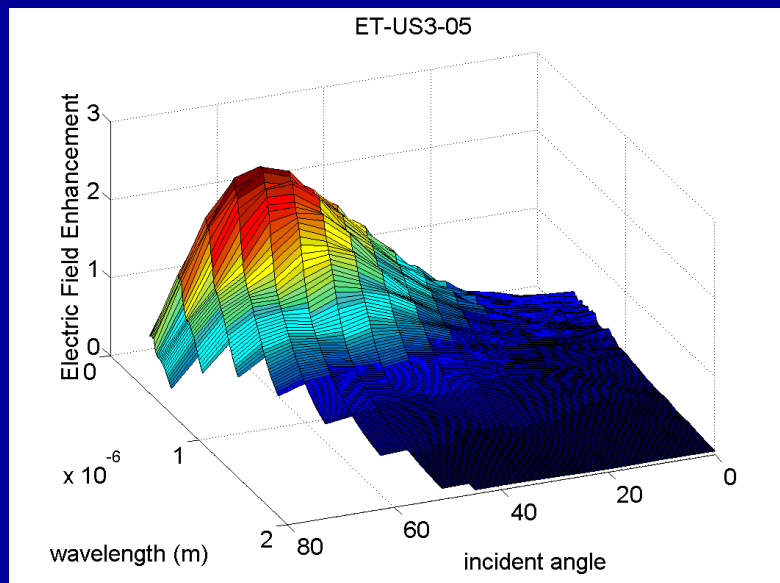
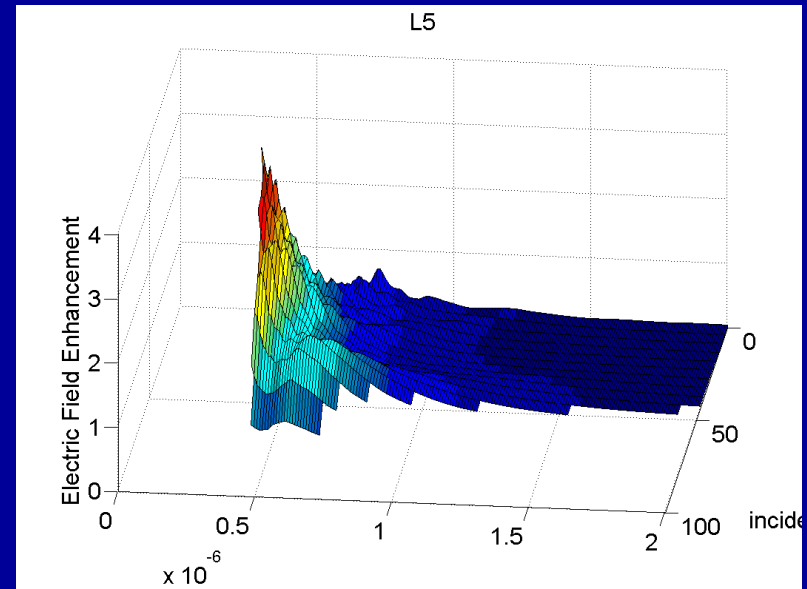
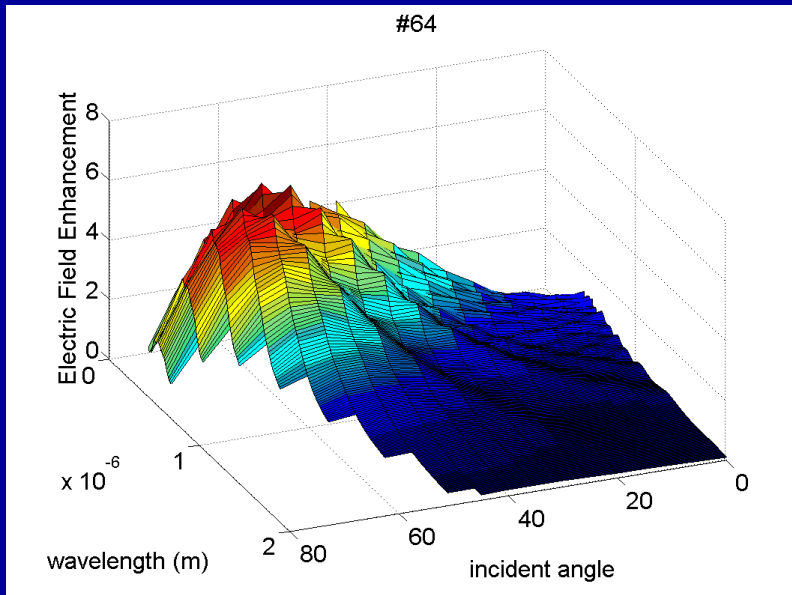


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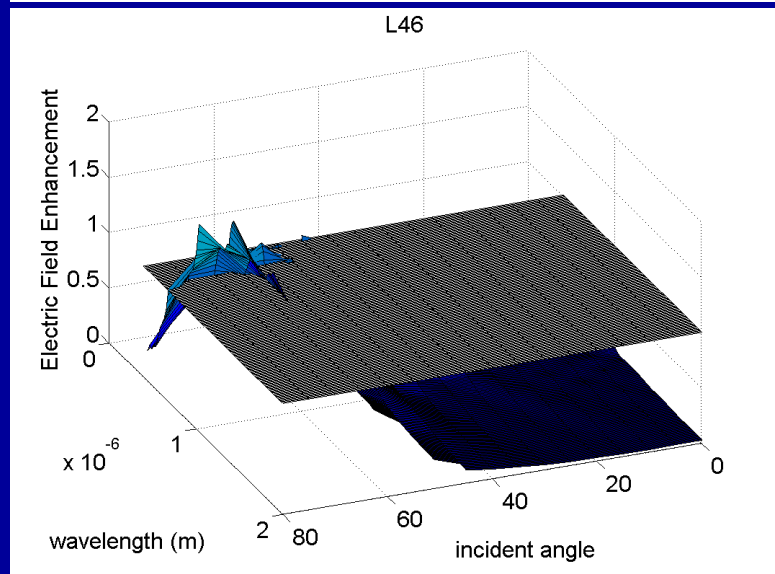
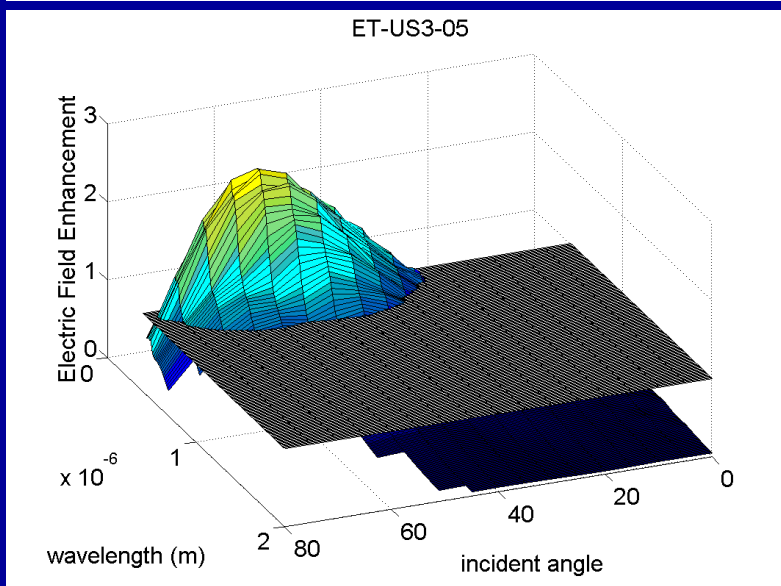
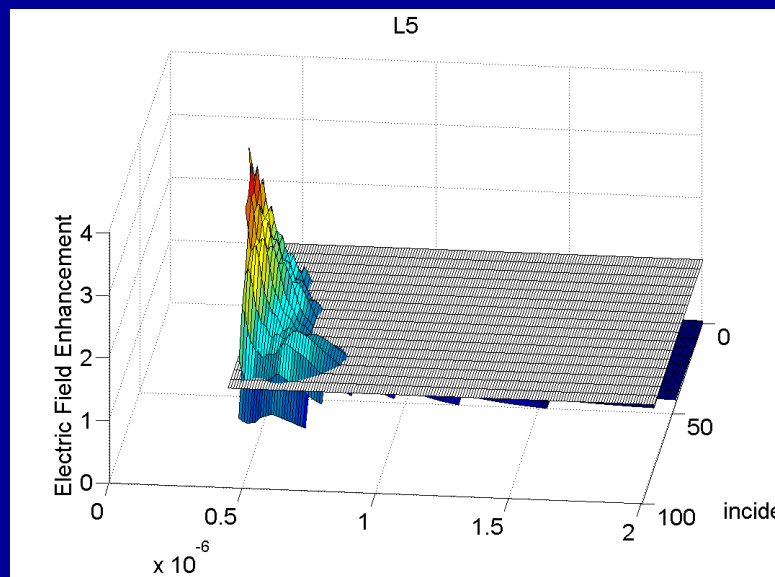
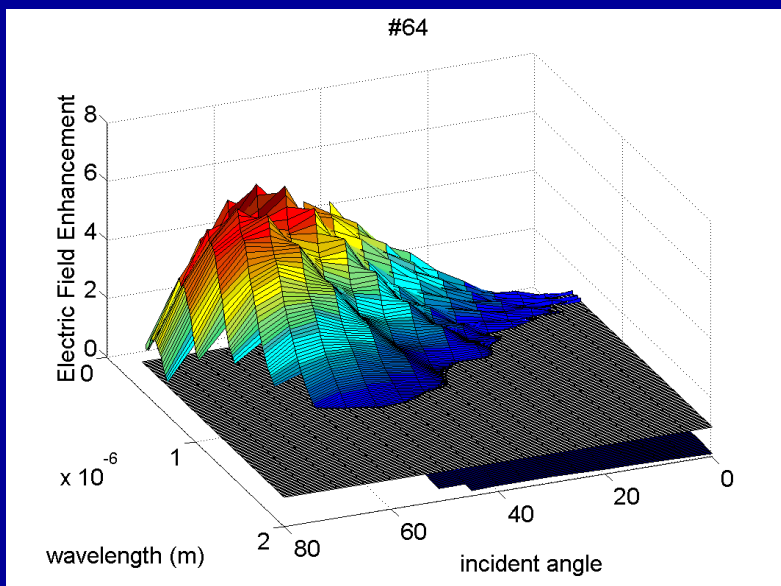
# Field enhancement (PdH)

excess heat samples



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excess heat samples



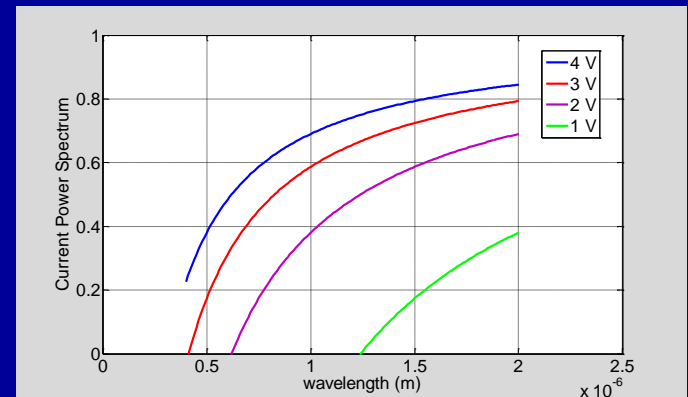
# What is the SP Driving Source?

*suggestion:*

Current fluctuations in the tunnel junction (MIM) [3]

- The metal/double layer/electrolyte interfaces as a MIM junction
- The power spectrum ( $C(\omega)$ ) is due to time fluctuations

$$C(\omega) = \frac{eV}{2\pi R_0} \left(1 - \frac{\hbar\omega}{eV}\right).$$



[3] R. W. Rendell and D. J. Scalapino, Phys. Rev. B 24, 3276 (1981)

# Results

- Pd foils can sustain excitonic modes
- Max electric field enhancement are order 10
- Current fluctuation at the double layer could drive plasmon excitations up to wavelenghts of fraction of micrometer

# Effect of morphology on electro-chemical kinetics

- The metal/electrolyte interface is dynamical
- Electrochemical reactions take place at the metal/electrolyte interface
- Their kinetics is affected by surface morphology:
  - The surface morphology is modified by electrochemical reaction (i.e. Pd dissolution/deposition reactions)
  - Reaction rates involving impurities may also be affected by surface morphology



# Example:

Change of the electrochemical kinetics of ions at planar or nano-spherical metal surfaces

$$\Delta G^\ddagger = \frac{(\Delta G + \lambda_{os})^2}{4\lambda_{os}}$$

(cfr. M. T. Spletzer, *Electrochimica Acta* **52** (2007) 2294-2301)

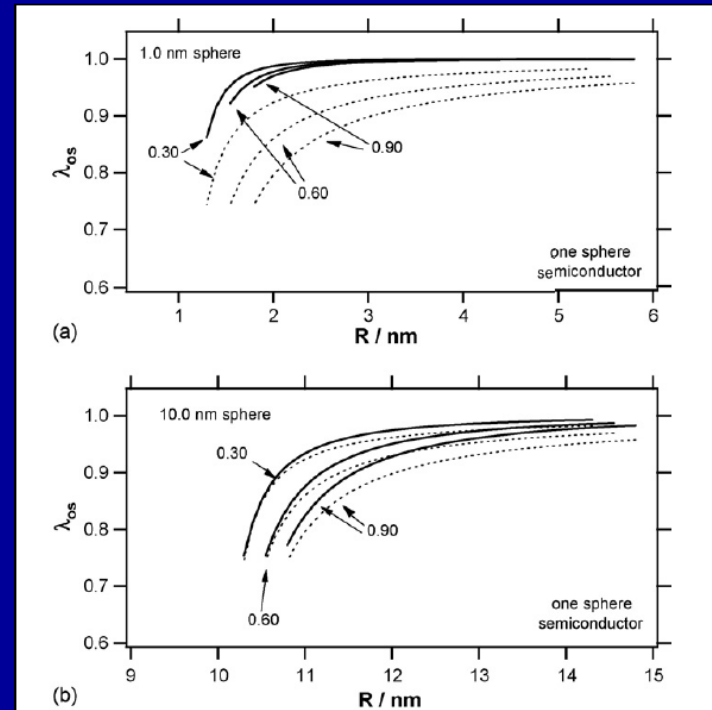
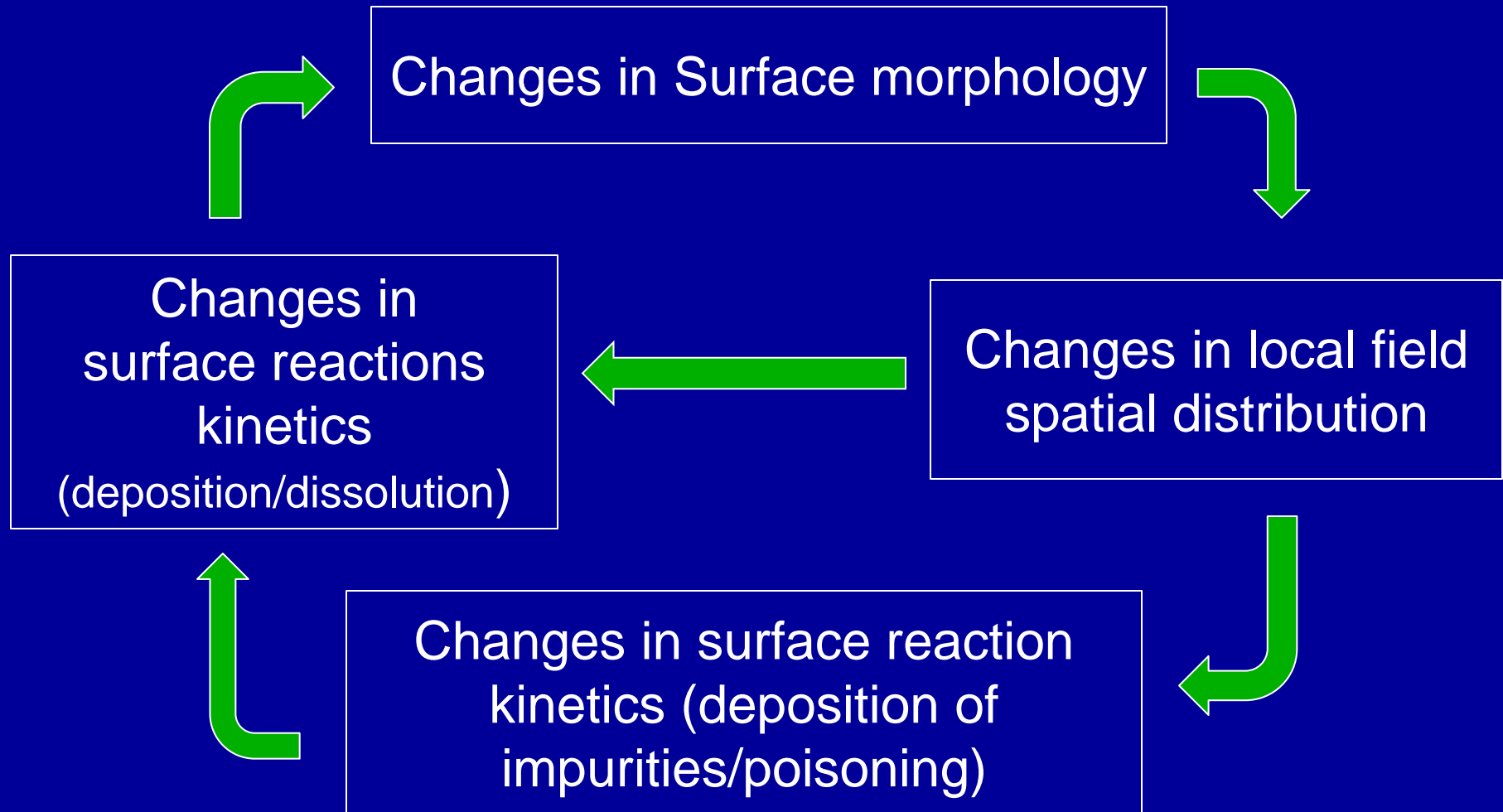


Fig. 2. (a)  $\lambda_{os}$  values calculated using Eq. (5) are shown for redox ions of radius 0.30, 0.60, and 0.90 nm (—) as they are stepped closer to a 1 nm semiconductor sphere. For each radius, the corresponding  $\lambda_{os}$  is also given for the ion at a planar semiconductor surface (---). (b)  $\lambda_{os}$  values calculated using Eq. (5) are shown for redox ions of radius 0.30, 0.60, and 0.90 nm (—) as they moved closer in steps to a 10.0 nm semiconductor sphere. For each radius, the corresponding  $\lambda_{os}$  is also given for the ion at a planar metal surface (---).

# Interplay between electrochemical kinetics and surface morphology



# Conclusions

The surface morphology of Pd cathodes has been characterized by atomic force microscopy, after electrochemical D loading.

The Electric field enhancement due to plasmon excitation has been estimated on the basis of the AFM images and their Power Spectrum

The results indicate that field enhancement can occur on samples giving excess heat.

# Conclusions

- The surface morphology play a role in changing the local e-m field at the cathode/electrolyte interface
- This mechanism could be accounted for when considering the electrochemical kinetics at the cathode, in particular in the case of nano-structured cathode surfaces
- Interplay between electrochemical kinetics and surface morphology has to be expected

***Thank you for your attention !***