Studies of electrocatalytic systems using X-ray absorption spectroscopy

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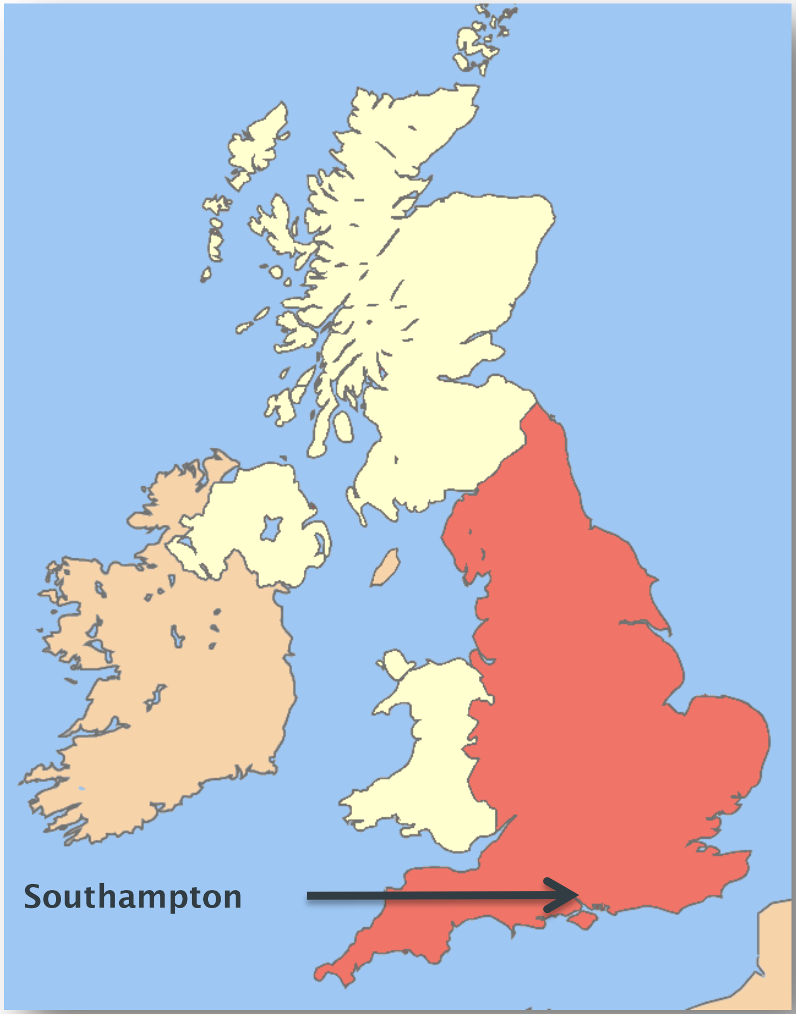
Overview



- Introduction
  - XAS theory, processing, analysis
  - Systems being studied
- Recent studies:
  - Dynamic Ru on Pt/C
  - Underpotential deposition (upd) of Cu on Au/C

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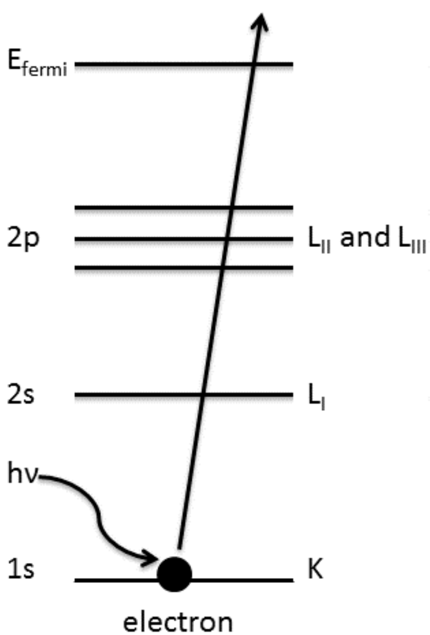
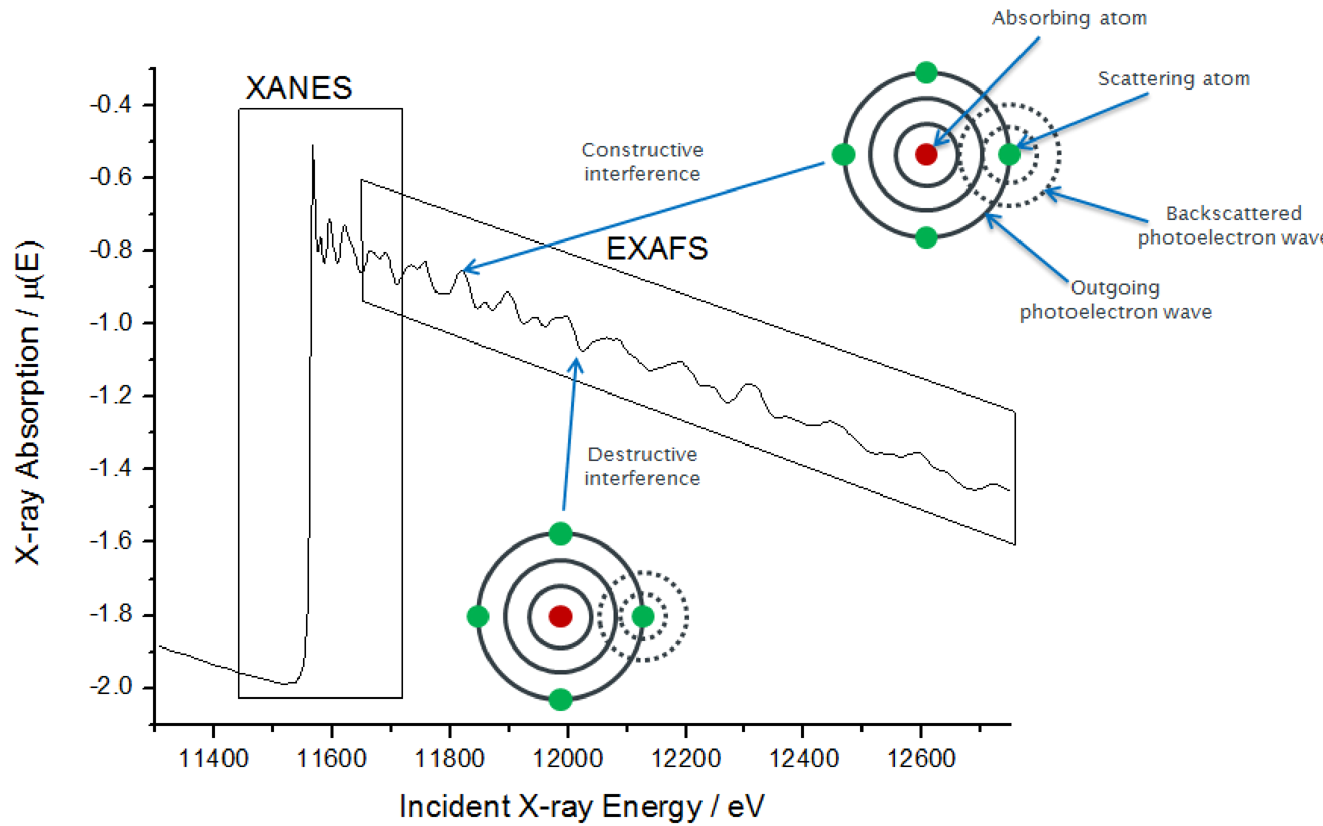
X-ray absorption spectroscopy

Origin of XAS effect

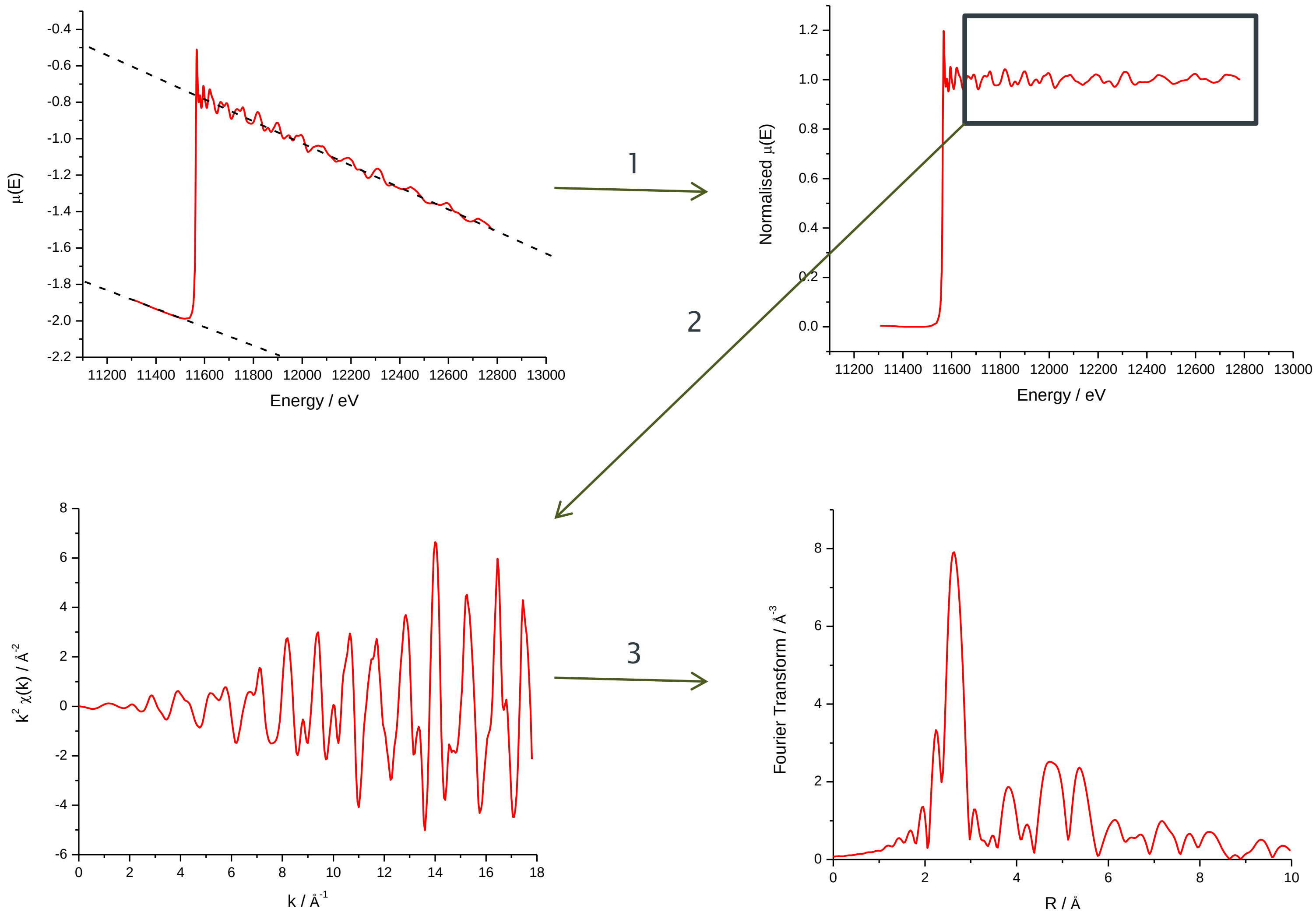




EXAFS - Extended x-ray absorption fine structure- Geometric information, e.g. coordination number, distance

XANES - X-ray absorption near edge spectroscopy- Electronic information

Data processing



Modelling EXAFS data

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin\left[2kR_j + \delta_j(k)\right]$$

$f_j(k)$ **and** ***$\delta_j(k)$*** are photoelectron scattering properties of the neighbouring atom (**determined theoretically**).

If these are known we can determine the following by **modelling** the data:

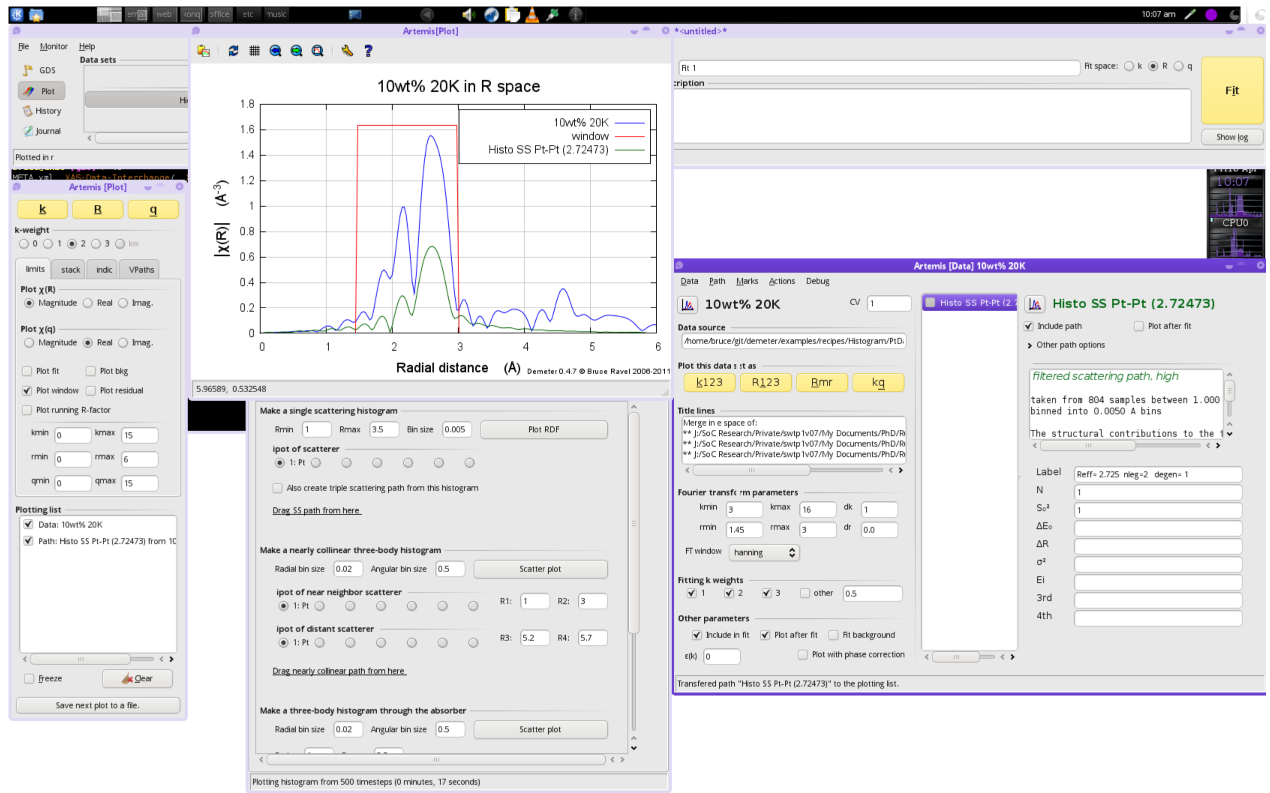
N_j coordination number of neighbouring atom

R_j distance to neighbouring atom

σ_j mean-square disorder of neighbour distance

Data Analysis

- Demeter package (Athena/Artemis) – Bruce Ravel
- Build structural model based on identity and distance of scattering atoms
- Per-atom average



B. Ravel, M. Newville, *J. Synchrot. Radiat.* **2005**, *12*, 537-541
http://cars9.uchicago.edu/ifeffit/Demeter

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Technique comparison

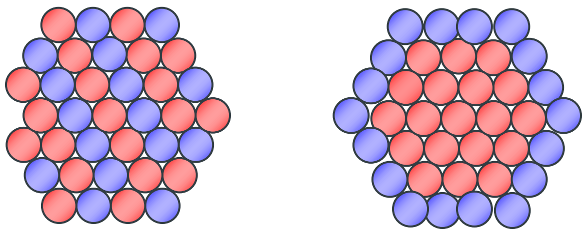
XRD

- Long range order
- Crystalline only
- Not element specific
- Able to distinguish different crystallographic sites and phases
- Averages different elements in the same crystallographic sites

XAS

- Short range structure
- Crystalline and amorphous
- Element specific
- Averages over all sites and phases
- Able to distinguish different elements in the same crystallographic sites (dopants)

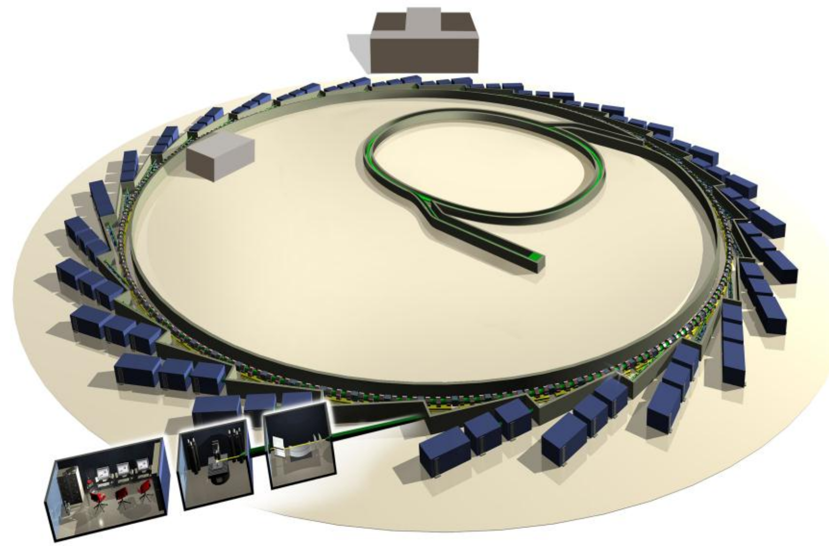
Data collected from perspective of both elements Allows core shell and alloy structures to be determined



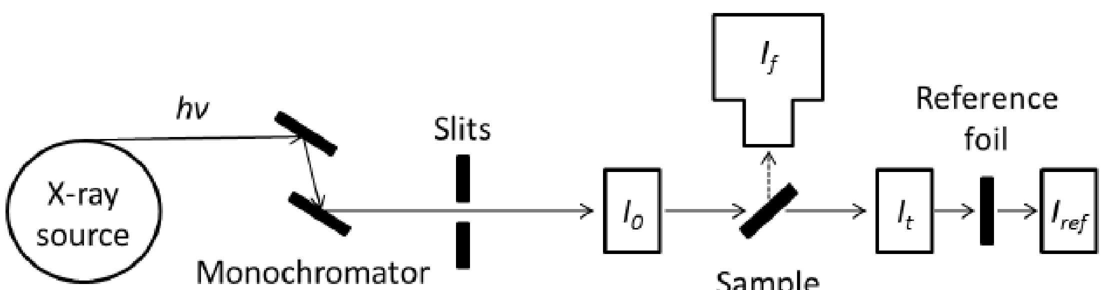
In situ XAS

- Versatile environments– solid, liquid, gas
- Operating conditions
    - Deposition/corrosion processes
    - Potential dependence of structure
    - Stability
    - Temperature
    - Pressure
- Can be combined with other techniques
    - XRD, IR, Raman, electrochemistry
- Time-resolved studies

Synchrotrons



Diamond Light Source, UK



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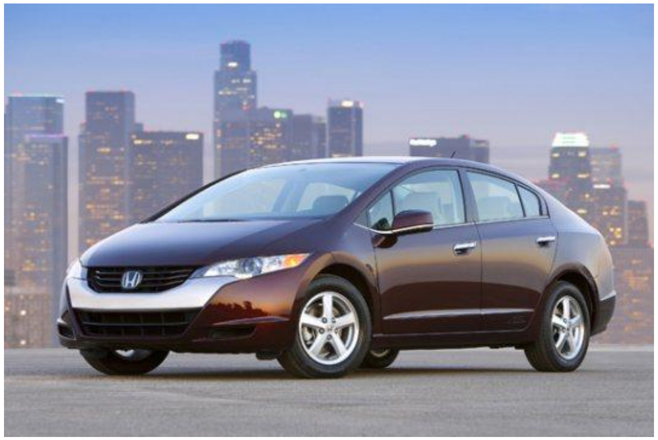
Electrocatalytic systems

PEM fuel cells



The Honda FCX Clarity

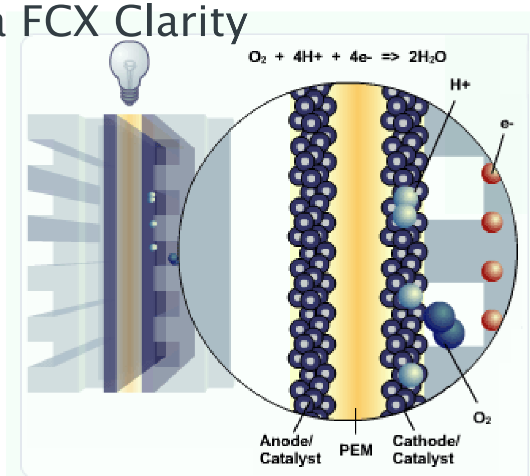
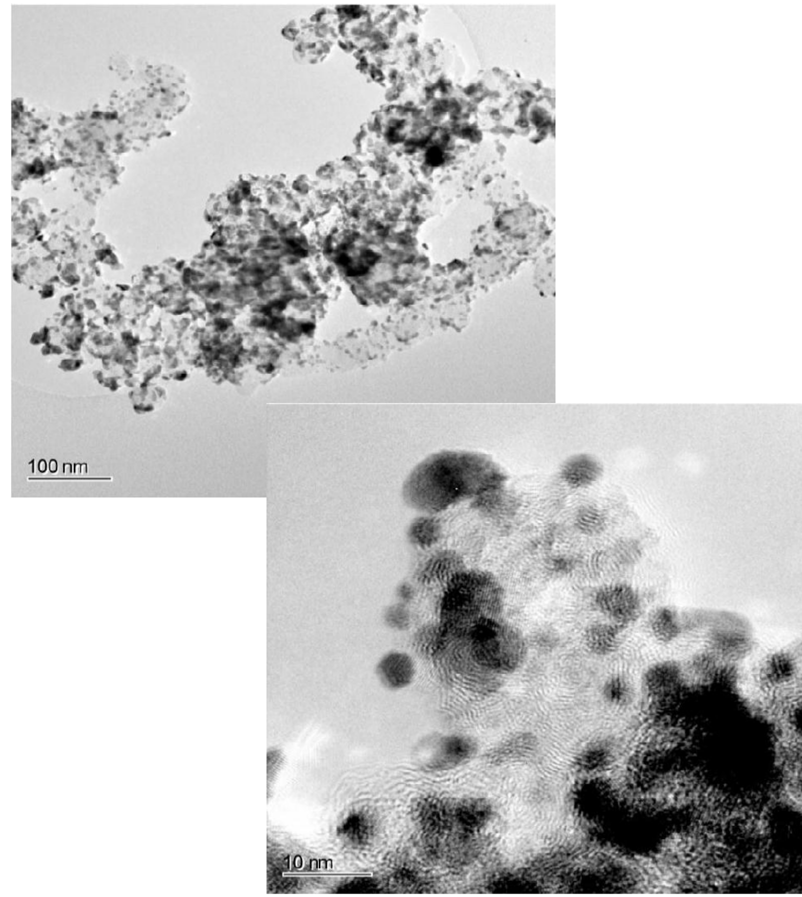


Figure: US DOE website
http://www1.eere.energy.gov/hydrogenandfuelcells/fc_animimation_process.html



TEM images of Pt/C catalysts

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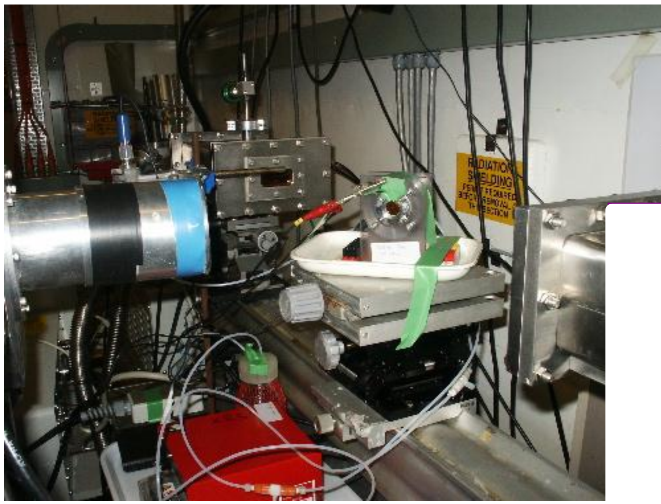
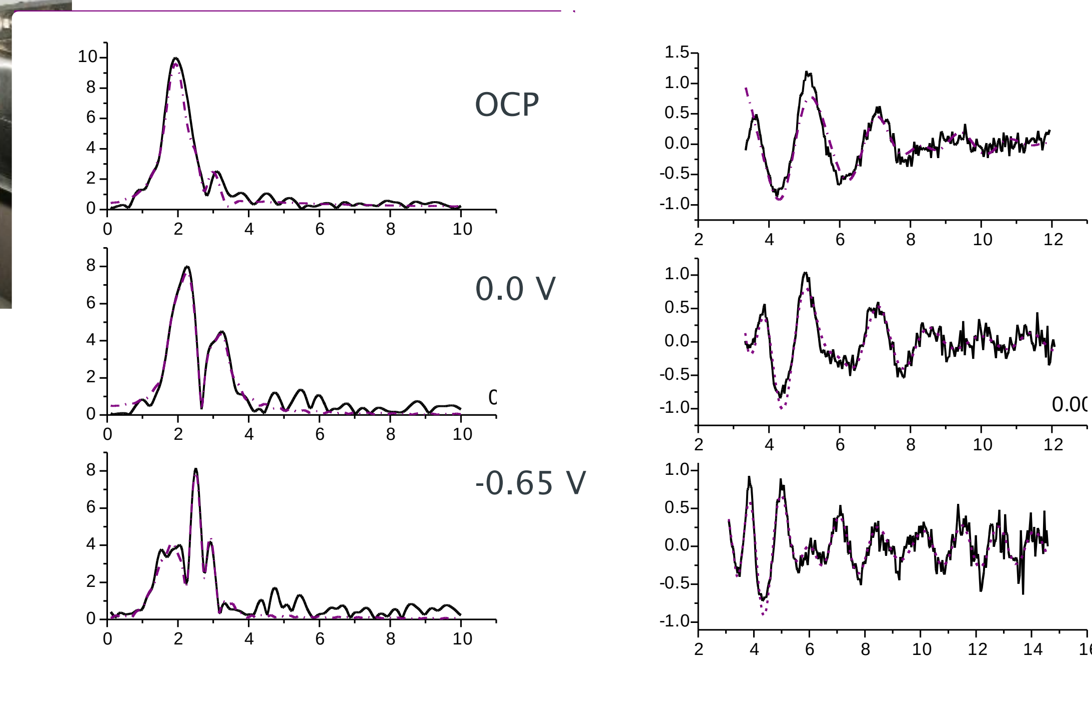
$Ru_{0.75\ ML}/Pt/C$



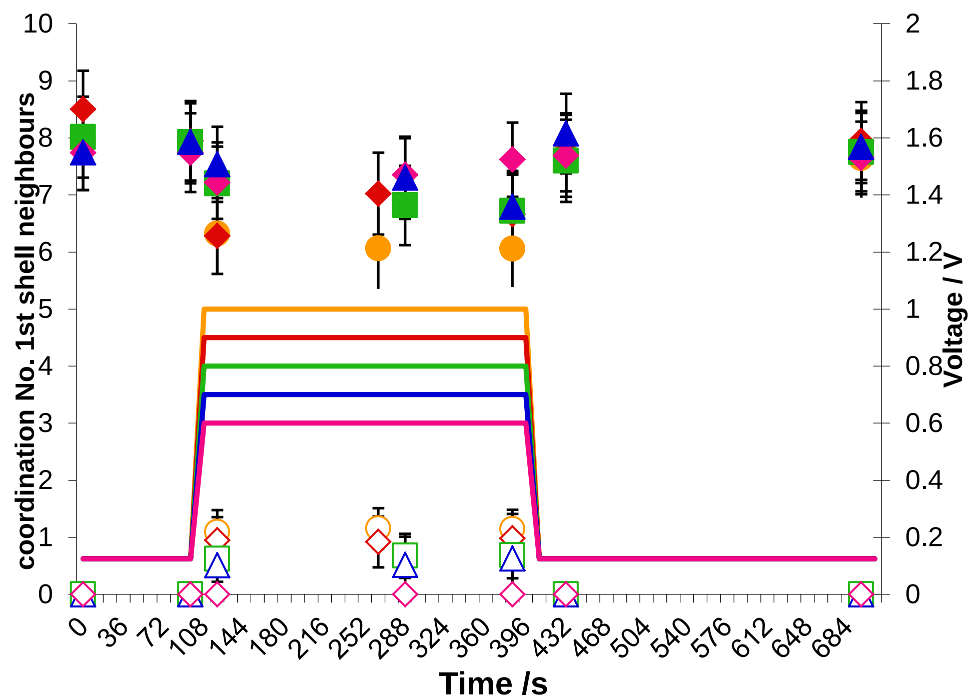
- Ru location as a function of potential
- Oxide shell → metallic alloy
- Ru migrates into particle
- Dynamic nature of surface previously neglected by theoretical models



Data is for $Ru_{0.75\ ML}/Pt/C$ catalyst at Ru K edge (SRS 16.5)

E. Crabb, A.E. Russell et al. PCCP, (2004) 6, 8, 1792-1798
A. Rose et al. Electrochimca Acta, (2009) 52, 18, 5556-5564

Operando studies (PEM electrolyte/fuel cell)



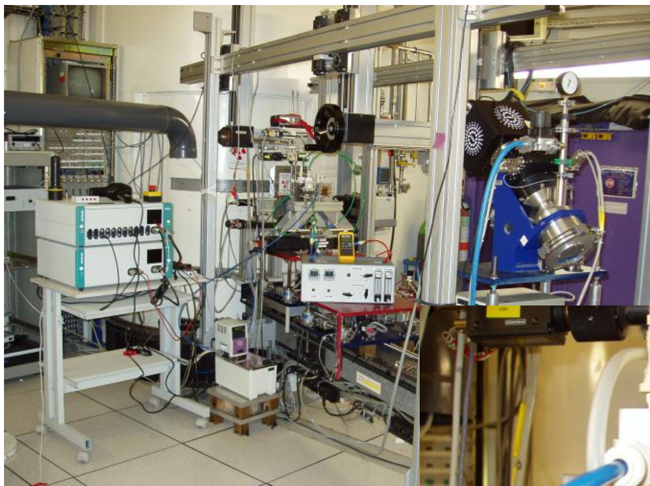
Time resolved Pt L_3 EXAFS (SRS 9.3). Pt/C cathode catalyst half cell (H_2|N_2 anode|cathode) conditions, 80 ° C

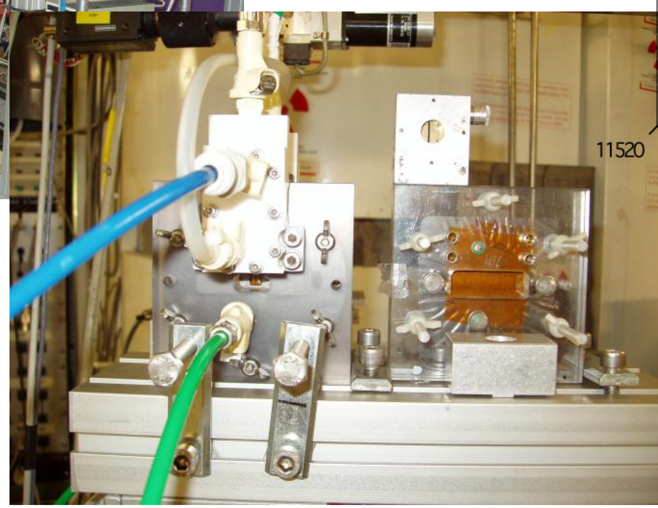
- For E > 0.7 V oxide growth, rapid change (within 20 s)
- Extent of oxide growth corresponds to two monolayers

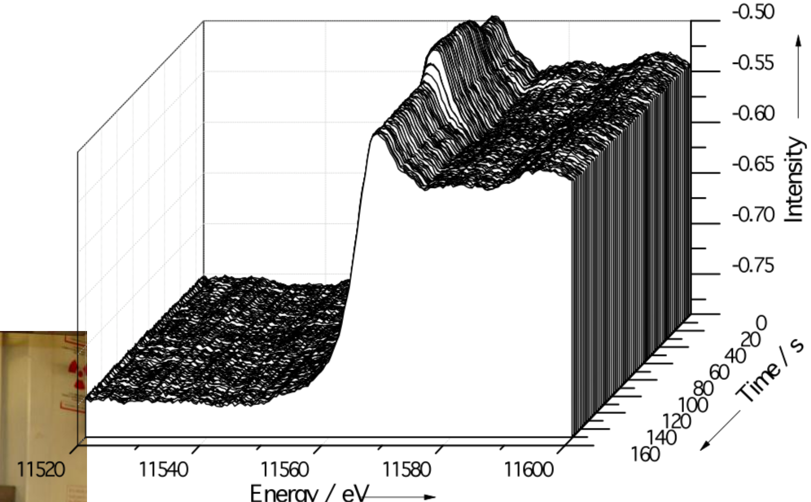
Hudson et al. ECS Transactions, (2010) 16, 2, 1395-1404

EDE at ESRF ID24

Enhanced time resolution= energy dispersive EXAFS







ESRF: ID24
in situ XAS PEM FC, with 10 ms time resolution.

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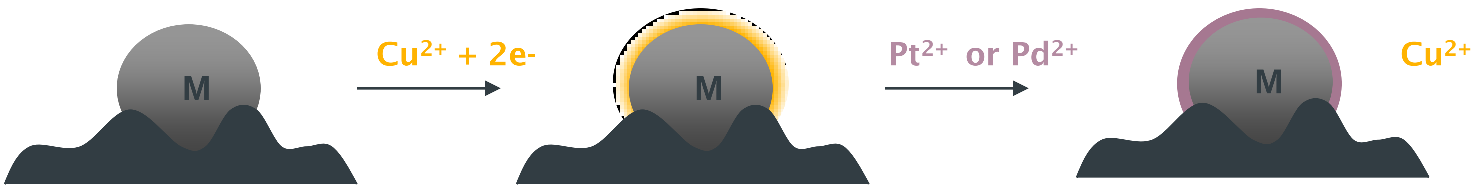
Core-shell electrocatalysts 1: Deposition of Pd/Cu on Au/C

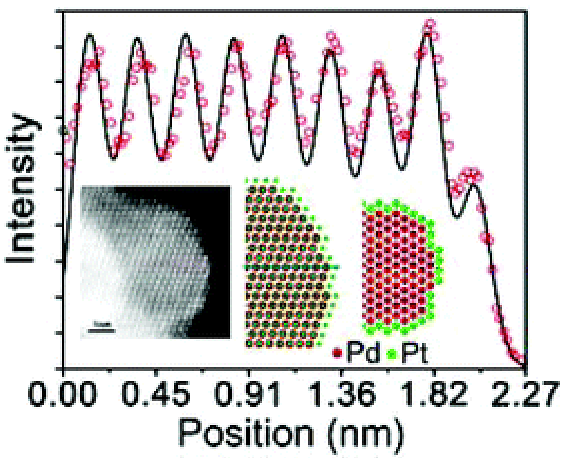
Preparation of core-shell catalysts

- Galvanic replacement of Cu upd layer



R.R. Adzic et al.

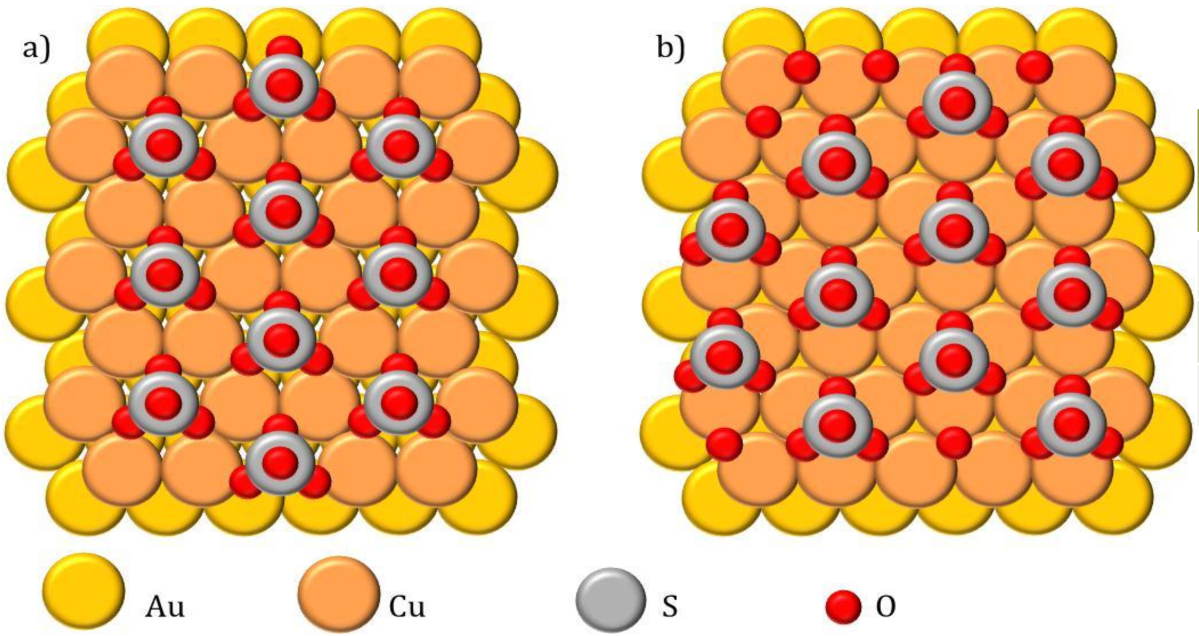
J. Phys. Chem. B., 109 (2005) 22701
Electrochem. Comm., 9 (2007) 2848
Electrocatalysis, 1 (2010) 213
J. Am. Chem. Soc. 131 (2009) 17298



Structure of Cu upd on Au

- From studies of single crystal surfaces

Initial $\Theta_{Cu} = 0.67$ Final $\Theta_{Cu} = 1$



hkl	1st shell CN	
	Cu-Cu	Cu-Au
111	6	3
110*	4	4
100*	4	4

Toney et. al. *Phys. Rev. Lett.* (1995) 75 , 4472.
Lee et. al. *J Phys. Chem. C*, (2009), 113, 12260
Kuzume et al. Electroanal. Chem. (2004), 570, 157.
Moller et al. Electrochim. Acta (1995), 40, 1259.
Cappadonia,et al. J. Electroanal. Chem. (1997), 436, 73

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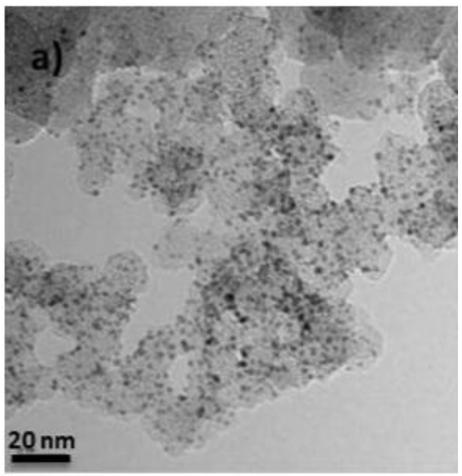
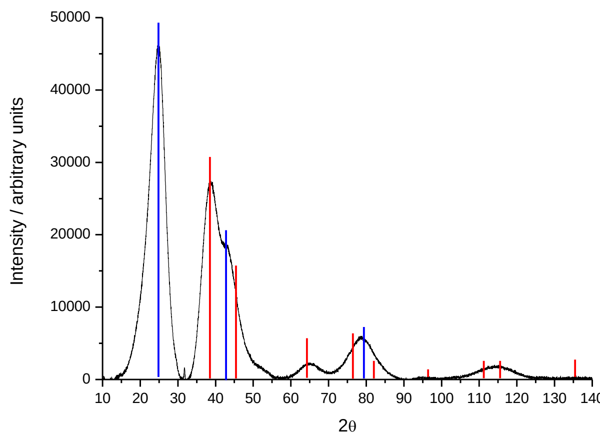
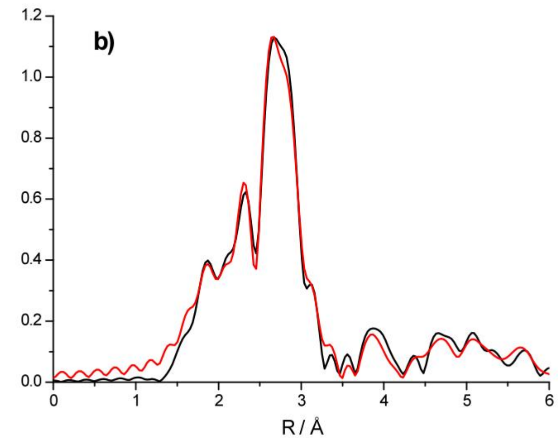
4 wt% Au/C

- Au nanoparticles prepared using thiol method of Brust et al. *J. Chem. Soc. Chem. Comm.* **1994**, 801.

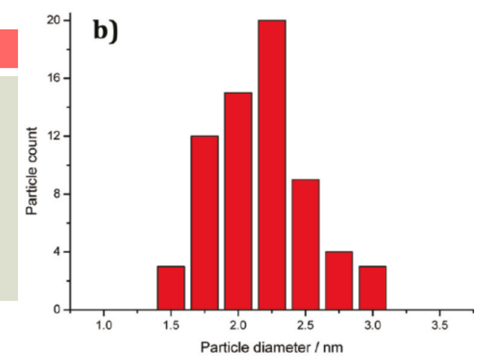




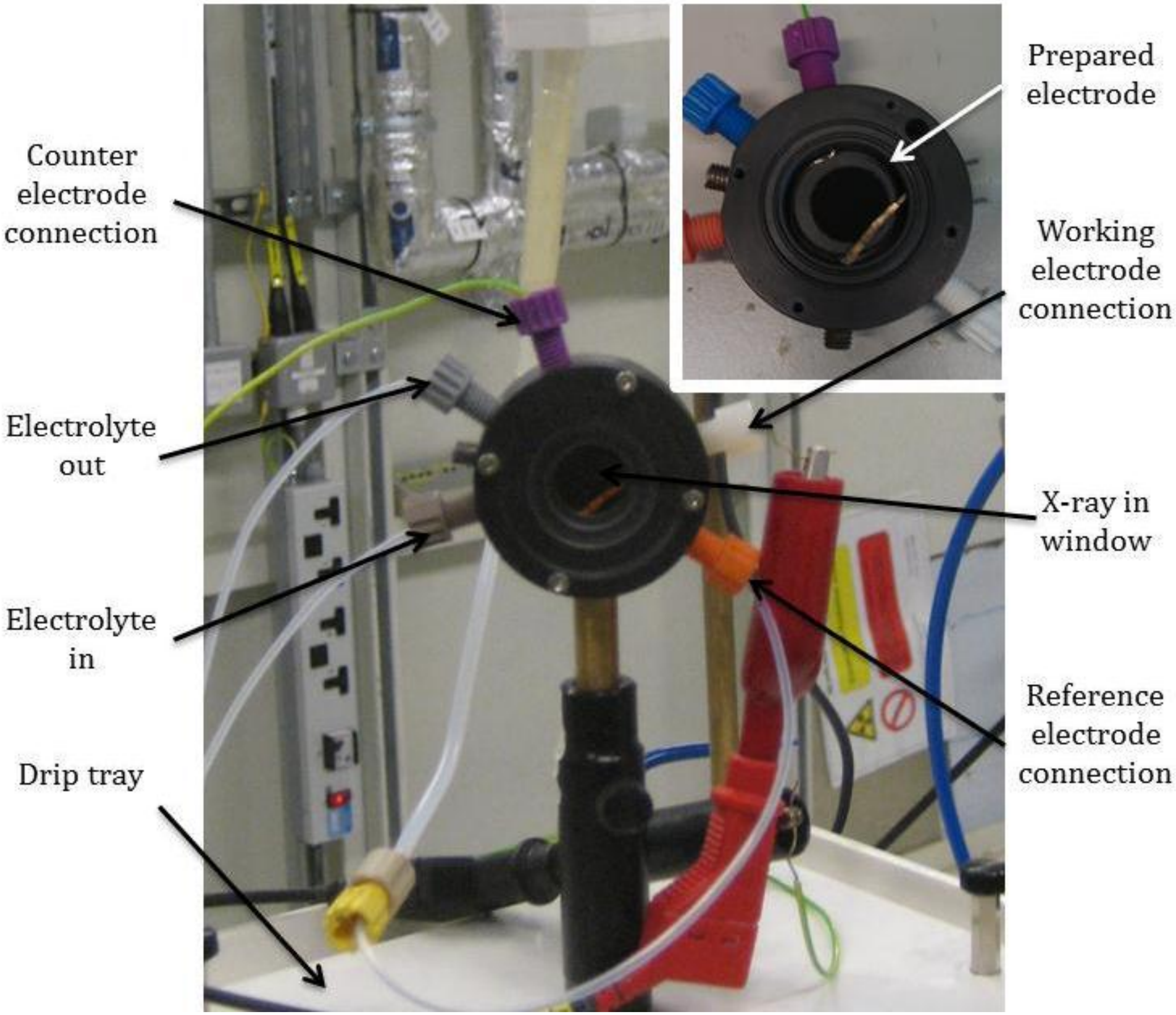


Ex situ EXAFS

Shell	N	R/Å	σ^2 x 10^4/ $Å^2$	ΔE_0/eV	R_f
$Au-Au_1$	6.9 ± 0.4	2.85 ± 0.01	56 ± 2	6.4 ± 0.3	0.017
$Au-S_1$	1.0 ± 0.3	2.31 ± 0.01	83 ± 37		
$Au-Au_2$	1.5 ± 0.7	4.03 ± 0.01	59 ± 25		
$Au-Au_3$	11.0 ± 3.8	4.94 ± 0.01	104 ± 23		



In situ cell



- Fast change over of electrolytes
- Versatile:

  Transmission XAS

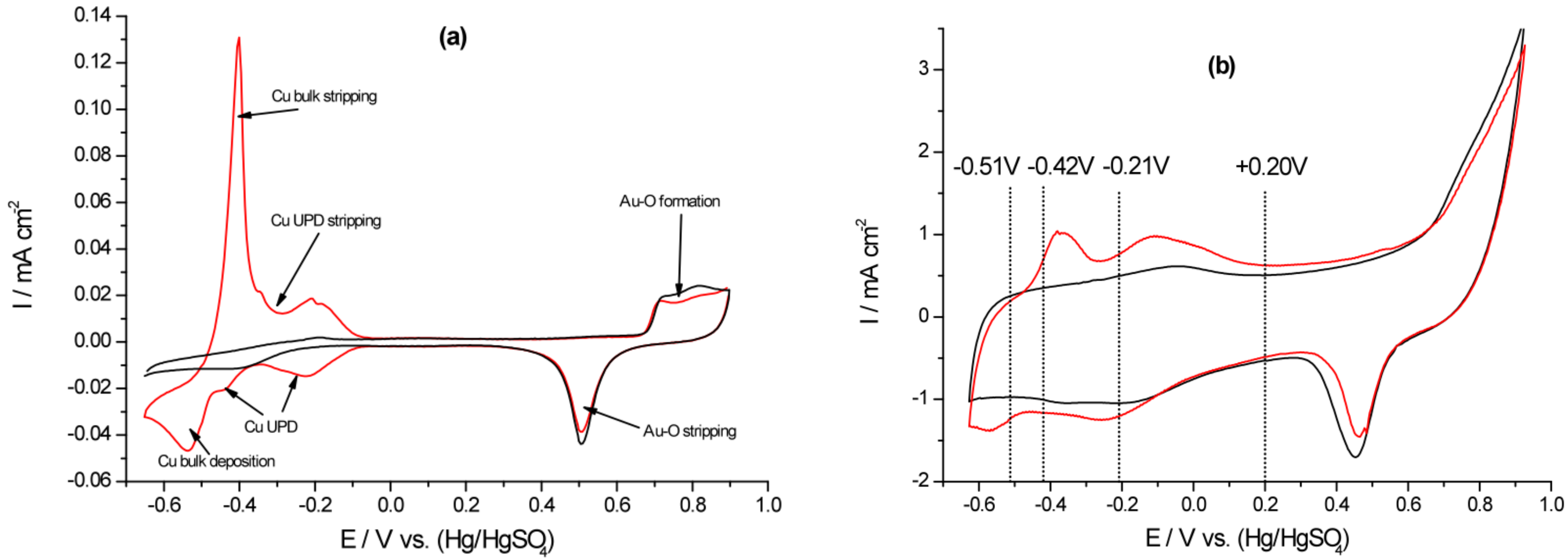
  Fluorescence XAS

  SAXS

  WAXS

Cu upd: voltammetry

- Comparing Cu upd on bulk Au and Au/C
  - Less clearly defined peaks



In EXAFS study:
-0.42 V = 0.44 ML
-0.51 V = 1.02 ML

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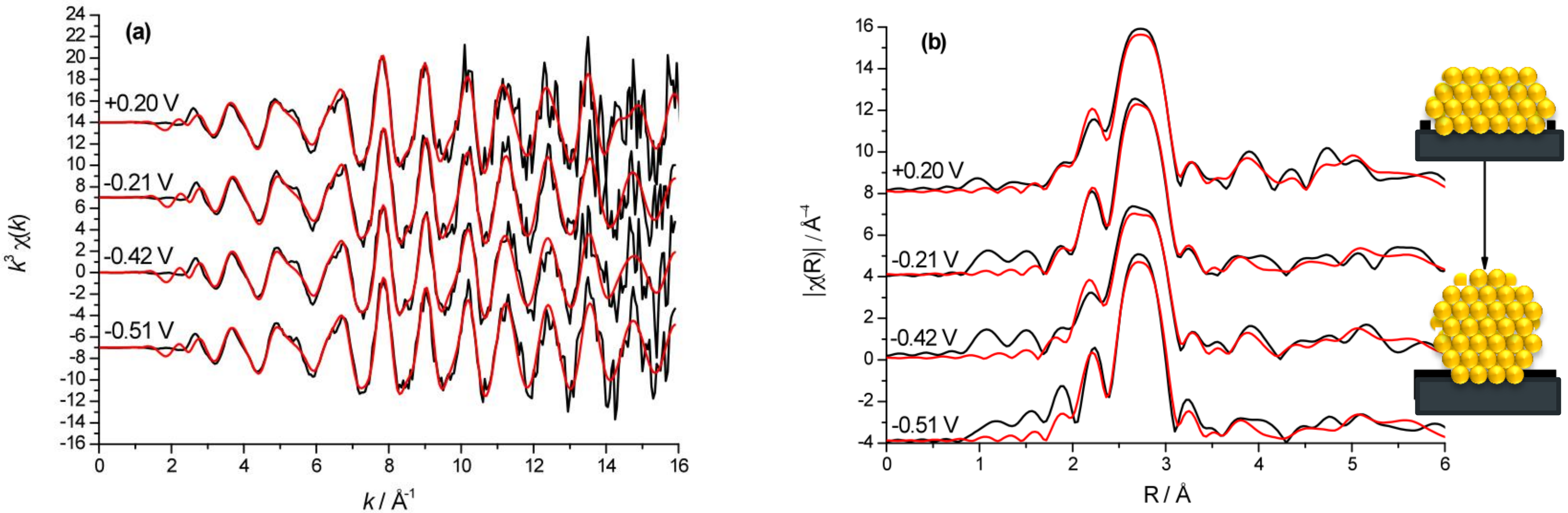
In situ EXAFS of Au/C – H_2SO_4



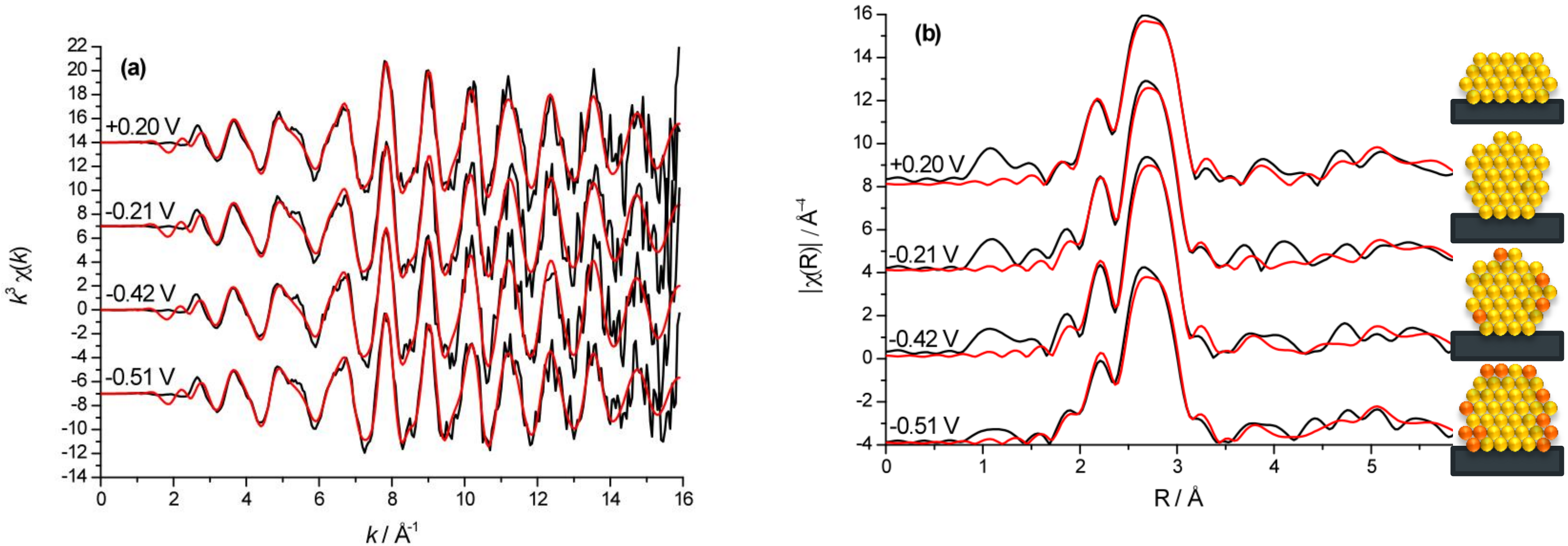
- No Au-S needed in fit, particles are ‘clean’
- Au-Au_1 is larger than *ex situ*, particles are larger

  Au-Au CN = 10.1
  → 3.5 nm

- Particle shape of Au/C is potential dependent
  - E = 0.2 V Au-Au_3/Au-Au_1 = 1, particles are flattened
  - E ≤ -0.21 V Au-Au_3/Au-Au_1 = 2, particles are spherical

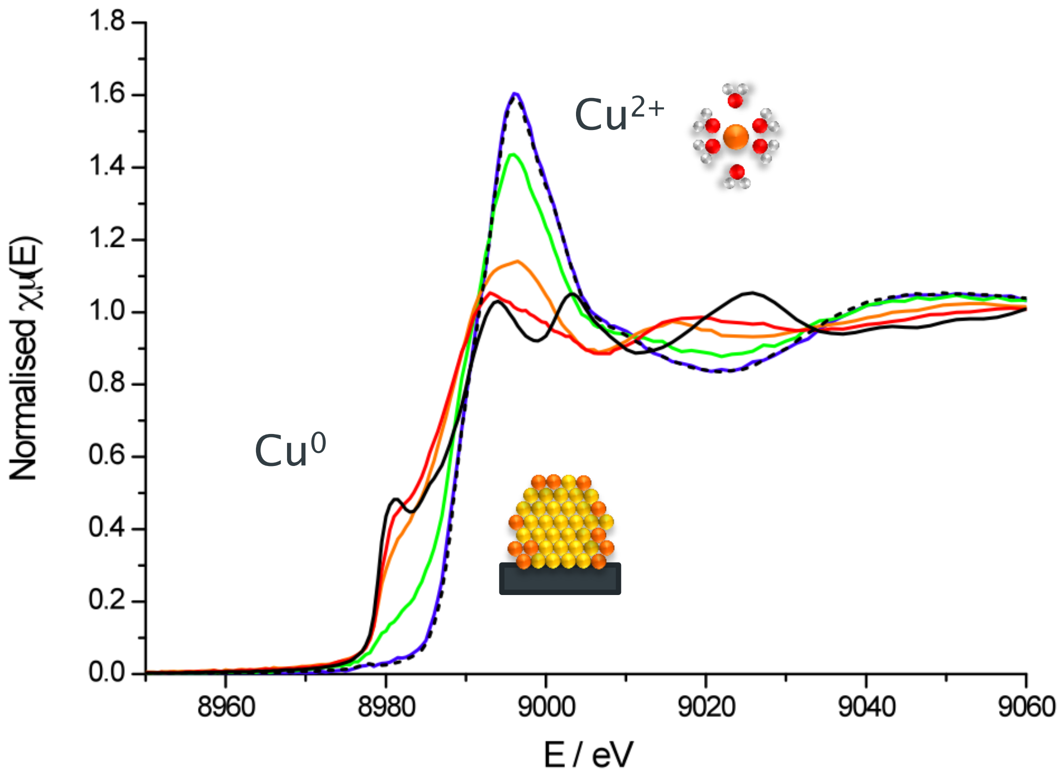
Cu upd: Au L_3 edge EXAFS – $CuSO_4 + H_2SO_4$

- Also shows shape change
- No evidence of Au-Cu in EXAFS



Cu upd: Cu K edge XANES

- Transition from Cu^{2+} to partially discharged Cu species



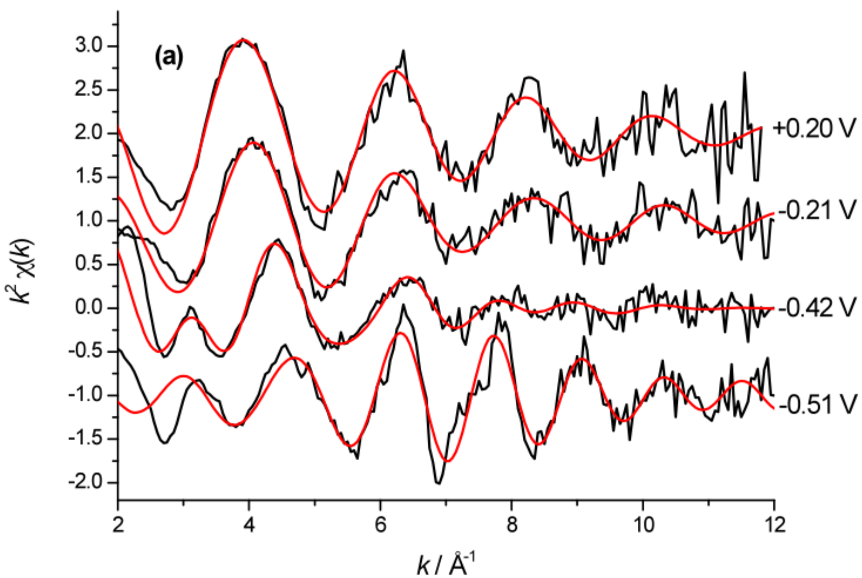
Cu^{2+} solution
+0.20 V
-0.21 V
-0.42 V
-0.51 V
Bulk Cu

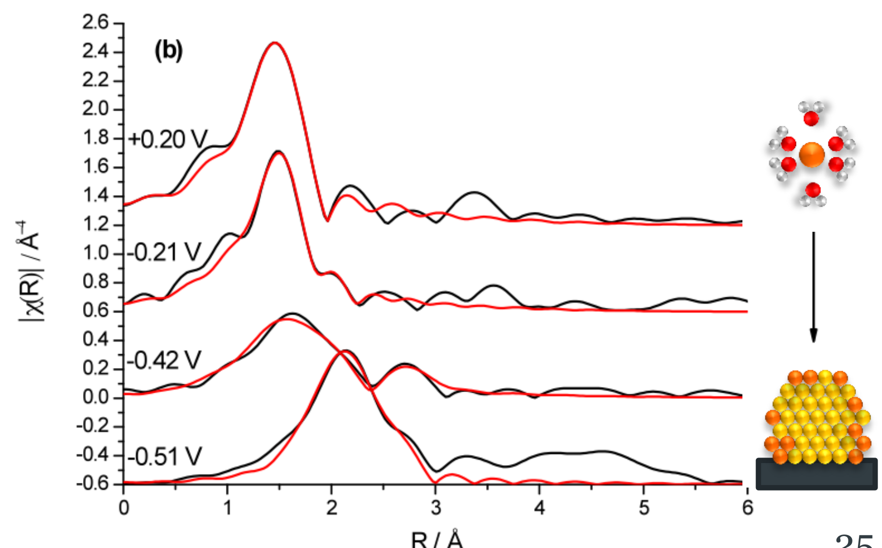
Lipkowski Electroanal. Chem. 1994, 365, 303

Cu upd: Cu K edge EXAFS

- +0.20 V and -0.21 V: octahedral Cu^{2+}
- -0.42 V: Cu-O and Cu-Au neighbours, but no Cu-Cu, $\theta = 0.44$
- -0.51 V: no Cu-O neighbours, Cu-Cu and Cu-Au found, $\theta = 1.02$

V vs. ($Hg/HgSO_4$)	Shell	*N*
+0.20	$Cu\text{-}O_{eq}$	4.5 ± 1.8
	$Cu\text{-}O_{ax}$	2.3 ± 0.9
-0.21	$Cu\text{-}O_{eq}$	3.2 ± 0.3
	$Cu\text{-}O_{ax}$	2.0 ± 0.2
-0.42	Cu-O	2.3 ± 0.9
	Cu-Cu	-
	Cu-Au	6.4 ± 2.4
-0.51	Cu-O	-
	Cu-Cu	2.6 ± 1.1
	Cu-Au	2.2 ± 1.1

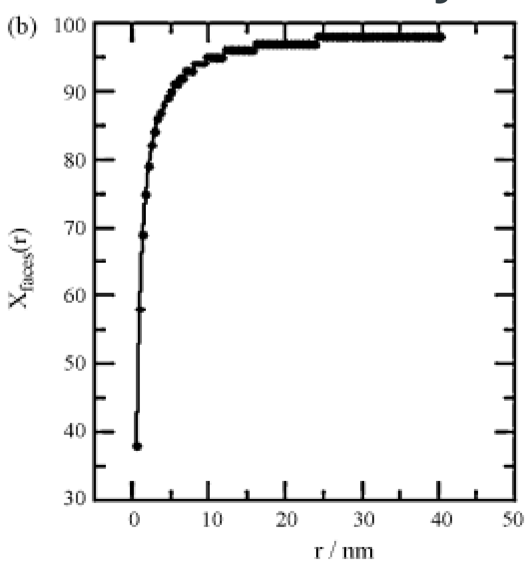


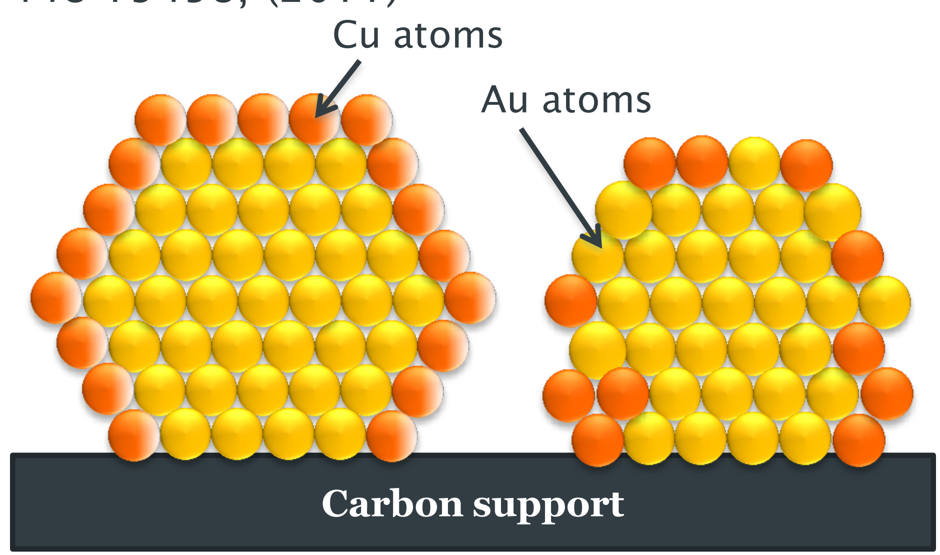


Structure of Cu upd on Au/C

- Potential dependence of Au/C
- Initial deposition at defects in outer shell of Au particles (no Cu-Cu neighbours) $\theta = 0.44$
- Full monolayer not achieved, further deposition as iclusters and/or slands decorating Au surface

✧ Price *et al.* JACS **133**, 19448-19458, (2011)





Oviedo, et al. *Electrochimica Acta* **2010**, *55*, 8244

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