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Title:	Theoretical study of electrochemical processes on platinum nanostructures
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Form 836 (7/06)

Theoretical study of electrochemical processes on platinum nanostructures

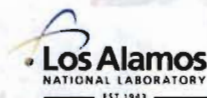Ivana Matanovic[a], Fernando Garzon[b] and Neil Henson[a]

[a] Los Alamos National Laboratory, Physics and Chemistry of Materials Group, New Mexico 87545, USA

[b] Los Alamos National Laboratory, Electronic and Electrochemical Materials and Devices Group, New Mexico 87545, USA

Future energy security concerns demand a transition from fossil-fuels to a more environmental benign energy sources. The use of fuel cells to directly convert chemical energy of fuels to electricity is a promising route for achieving this. Efficient fuel cell performance however requires the engineering of platinum group metal catalysts with higher mass activity and more stability. Along that line, we have undertaken a comprehensive and systematic study of the structure, reactivity and stability of different single and multi-walled platinum nanotubes using the plane wave, pseudopotential implementation of DFT. The change in the catalytic activity of the nanomaterial induced by the structural changes (size and the chirality) is studied by calculating equilibrium adsorption potentials for oxygen reduction reaction (ORR) intermediates and by constructing free energy diagrams in the ORR dissociative mechanism network. In addition, the stability of the platinum nanotubes both in gas and aqueous environment is investigated in the terms of relative electrochemical dissolution shifts and by determining the most stable state of the material as a function of pH and potential as represented in Pourbaix diagrams.

Theoretical study of electrochemical processes on platinum nanostructures

Ivana Matanović, Fernando Garzon, Neil Henson

Physics and Chemistry of Materials

Los Alamos National Laboratory, Los Alamos, USA

Motivation

Reducing the ORR overpotential / cost:

(1) alloying platinum with platinum group metals

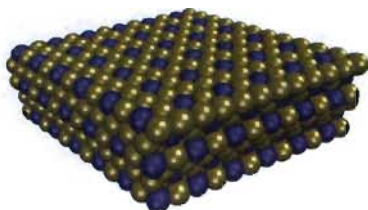**(2) nanostructures:** nanotubes and nanoparticles
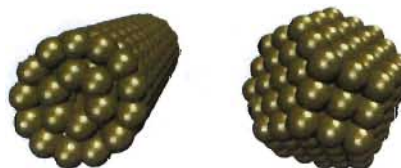
Figure: Pt₃Ni(111) surface

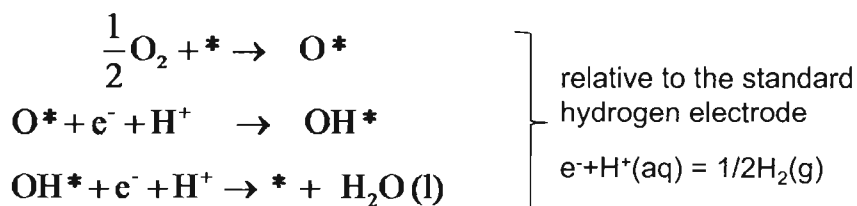Figure: (6,6)@(13,13) MWPtNT nanotube and 2nm Pt₂₀₁ cluster

Motivation

study the influence of alloying component **concentration and distribution** on the **ORR activity** and **stability** in aqueous environment

study the effect of **size and structure** of a nanomaterial on the ORR activity and stability in aqueous environment

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Methodology - study of ORR mechanism

Reactions connecting different states of the metal surface(*) in the ORR mechanism

$$\frac{1}{2}O_2 + * \rightarrow O*$$
$$O* + e^- + H^+ \rightarrow OH*$$
$$OH* + e^- + H^+ \rightarrow * + H_2O\,(l)$$

relative to the standard hydrogen electrode

$e^- + H^+(aq) = 1/2 H_2(g)$

Free gibbs energy of the reactions (Norskov et al. J. Phys. Chem. B 2006, 110, 21833)

$$\Delta G_{w,water} = \Delta E_{w,water} + \Delta ZPE + T\Delta S$$

$$\Delta G(U, pH, T = 298K) = \Delta G_{w,water} \underbrace{- eU} + \underbrace{kT\ln(10)pH}$$

bias effect   correction for the free energy of H+

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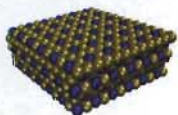
Oxygen Reduction Reaction on Pt-Ni alloys

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Conclusions

- catalytic activity – modification in the electronic structure induced by the specific subsurface composition

- the ORR overpotential was found to decrease

$$Pt < Pt_3Ni < PtNi_3 < PtNi$$

confirmed experimentally, ECS 220th meeting, Boston, NIST group

dx.doi.org/10.1021/jp111930w | *J. Phys. Chem. C* 2011, 115, 10640–10650

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Conclusions

shifts in the electrochemical dissolution potentials relative to Pt:

PtNi

- the least susceptible to corrosion

Pt$_3$Ni

- most susceptible to electrochemical dissolution of Pt monolayer
- most susceptible to poisoning of the surface by the formation of nickel oxide

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Oxygen Reduction Reaction on Pt nanotubes

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carbon nanotubes, 90'

AFM probe tips

DNA sequencing
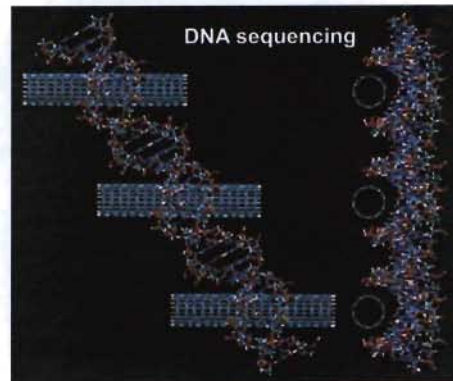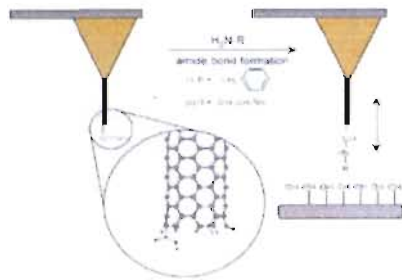
(bio)sensing, imaging, nanoelectronics

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metal nanotubes, 2000'

- magic "structure" and conductance - nanoelectronics

- Au, Ag nanotubes less then 2nm thickness have been synthesized by an electron-beam technique in an UHV-TEM

1 nm ▬
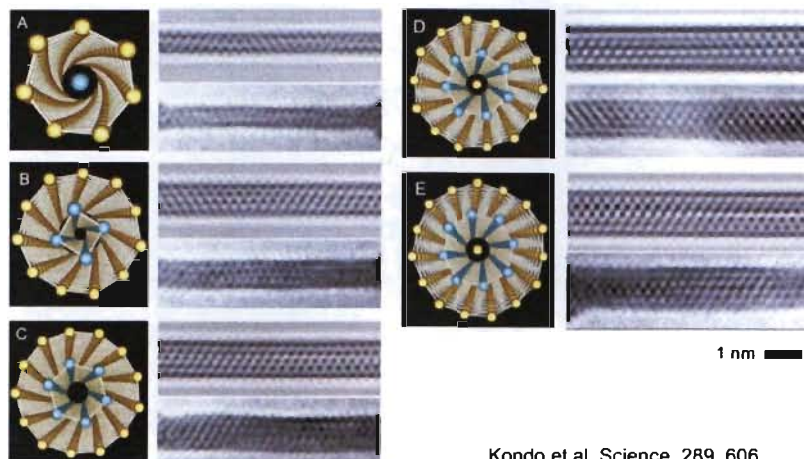
Kondo et al. Science, 289, 606

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metal nanotubes, 2000'

- Pt nanotubes – 1.0 and 0.5 nm in diameter

0.5 nm – six atomic rows coiling around tubes axes

 1 nm   - 13-6 multishell structure
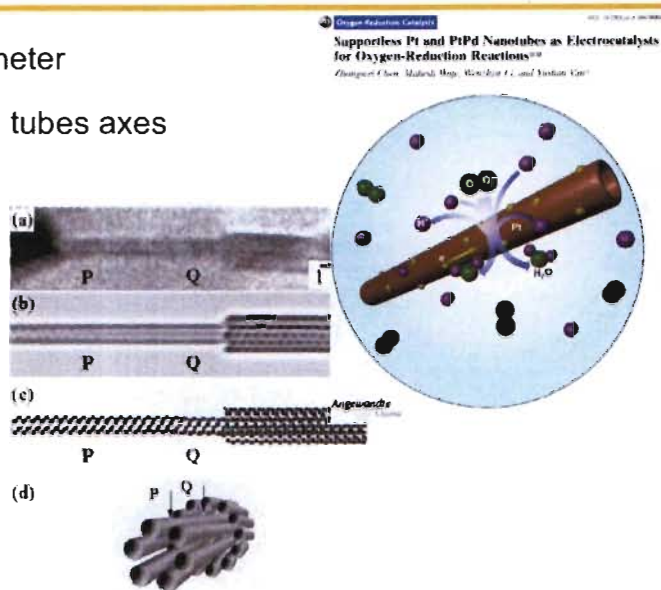
Figure: HR-TEM image of platinum nanotube
Y. Oshima et. al, Phys. Rev. B, 65, 121401 (2002)

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Pt nanotubes

PtNT: Rolling-up Pt(111) sheet to form a tube
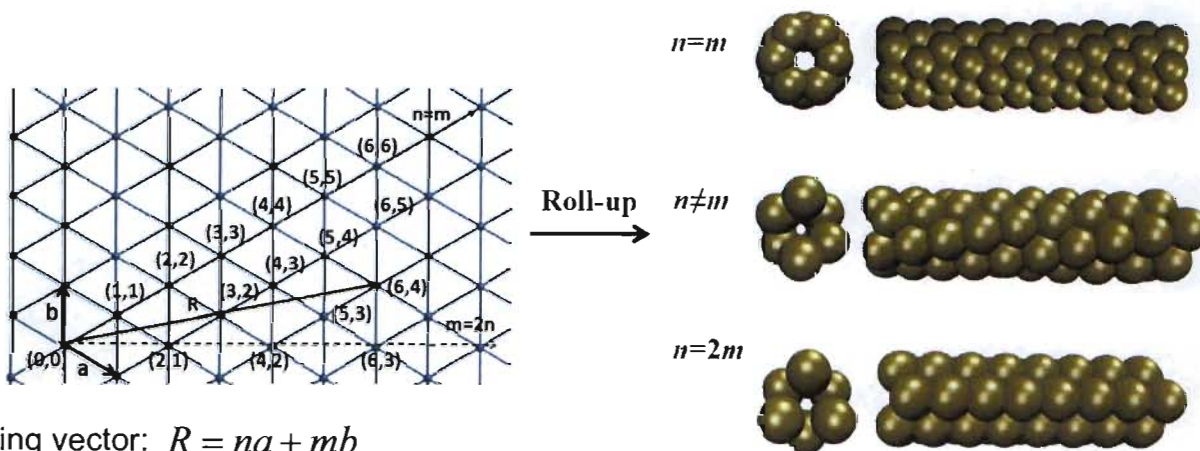
rolling vector: $R = na + mb$

$$r = \frac{\sqrt{2}a_c}{4\pi}\sqrt{n^2 + m^2 - nm}$$

a_c = 3.70- 3.85 Å

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Pt nanotubes

(6,6) (6,3)
(8,8) (8,4)
(9,9) (10,5)
(10,10) (12,6)
(11,11) (14,7)
(12,12) (16,8)
(13,13) (18,9)
(15,15) (20,10)
(18,18) (24,12)
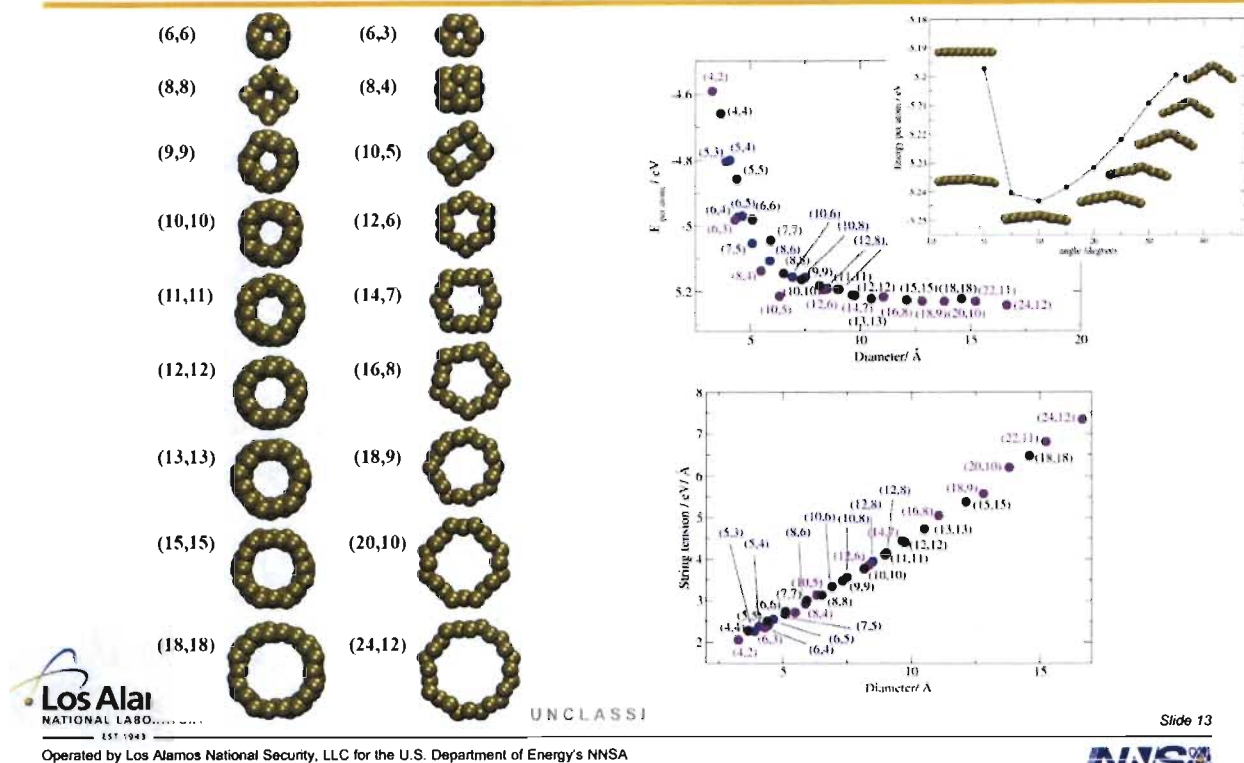
Pt nanotubes + oxygen

Table. Adsorption energies in eV and a shift in equilibrium adsorption potential in V for oxygen on the fcc site for different nanotubes and coverages

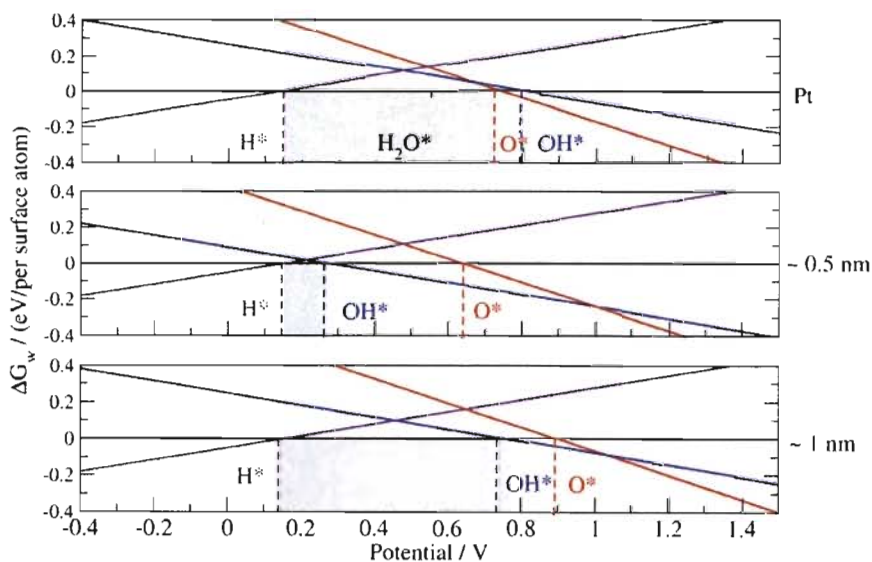|		0.25 ML		0.33 ML		0.5 ML	
		E_{ad}	ΔU_f	E_{ad}	ΔU_f	E_{ad}	ΔU_f
	Pt	-4.42	0.00	-4.25	0.00	-4.07	0.00
≈ 0.5 nm	(6,3)	-4.72	-0.15	-4.52	-0.14	-4.50	-0.22
	(6,4)	-4.70	-0.14	-4.31	-0.03	-4.44	-0.19
	(6,6)	-4.72	-0.15	-4.41	-0.08	-4.46	-0.20
≈ 1 nm	(12,6)	-4.29	+0.07	-3.98	+0.14	-3.96	+0.06
	(12,8)	-4.29	+0.07	-4.03	+0.11	-4.00	+0.04
	(12,12)	-4.18	+0.12	-3.94	+0.16	-3.97	+0.05
	(13,13)	-4.14	+0.14	-3.90	+0.17	-3.92	+0.08
	(6,6)@(13,13)	-4.05	+0.19	-4.21	+0.02	-4.06	+0.05

Pt nanotubes + hydroxyl

Table. Adsorption energies in eV and a shift in equilibrium adsorption potential in V for hydroxyl on the atop site for different nanotubes and coverages
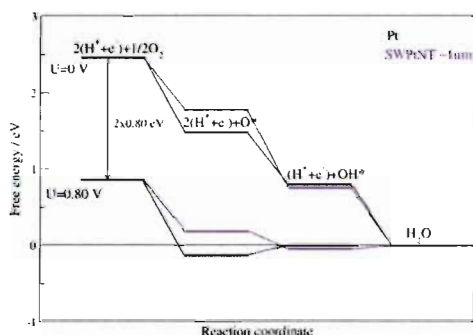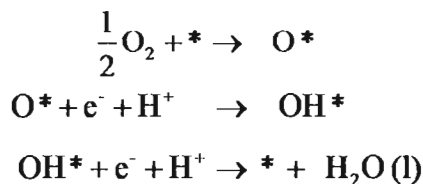
		0.25 ML		0.33 ML		0.5 ML	
		E_{ad}	ΔU_f	E_{ad}	ΔU_f	E_{ad}	ΔU_f
	Pt	-2.88	0.00	-2.92	0.00	-3.09	0.00
≈ 0.5nm	(6,3)	-3.70	-0.82	-3.47	-0.55	-3.76	-0.67
	(6,4)	-3.60	-0.72	-3.35	-0.43	-3.69	-0.60
	(6,6)	-3.54	-0.66	-3.54	-0.62	-3.52	-0.43
≈ 1nm	(12,6)	-2.92	-0.04	-2.98	-0.06	-2.73	+0.36
	(12,8)	-2.89	-0.01	-2.98	-0.06	-2.73	+0.36
	(12,12)	-2.89	-0.01	-2.97	-0.05	-2.91	+0.18
	(13,13)	-2.83	+0.03	-2.87	+0.03	-2.85	+0.24
	(6,6)@(13,13)	-3.07	-0.19	-3.13	-0.21	-3.20	-0.11

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Pt nanotubes phase diagram

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Dissociative oxygen reduction reaction (ORR) mechanism

$$\frac{1}{2}O_2 + * \rightarrow O*$$

$$O* + e^- + H^+ \rightarrow OH*$$

$$OH* + e^- + H^+ \rightarrow * + H_2O\,(l)$$

Figure: Free-energy diagrams for ORR over Pt(111) surfaces and SWPtNT for cell potentials U=0.80 V

PtNTs, d ~ 1nm

smaller ORR overpotential than Pt(111), up to 100 meV

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Dissociative oxygen reduction reaction (ORR) mechanism

$$\frac{1}{2}O_2 + * \rightarrow O*$$

$$O* + e^- + H^+ \rightarrow OH*$$
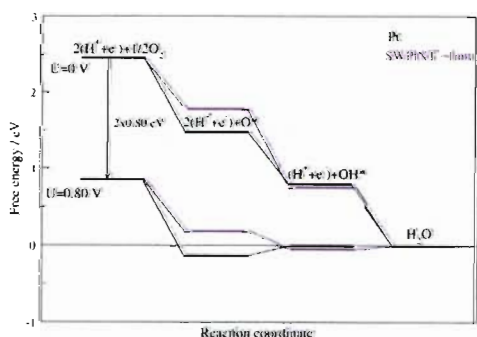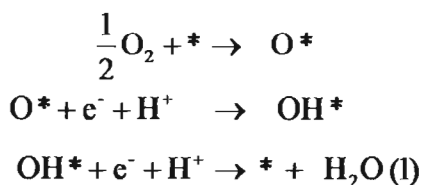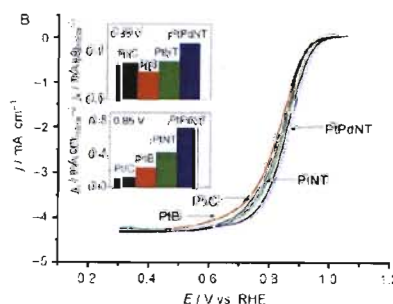
$$OH* + e^- + H^+ \rightarrow * + H_2O\,(l)$$

Figure: Free-energy diagrams for ORR over Pt(111) surfaces and SWPtNT for cell potentials U=0.80 V

In need for measurements – ORR curves

Chen et al, Angew. Chem. Ind. Ed. 2007, 46, 4060

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Stability of the surfaces

What about the stability of these nanostructures?

Electrochemical dissolution can severely decrease the performance of the material

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Stability of the surfaces

Estimate of the shift in the electrochemical dissolution potential

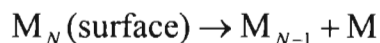$$M_N(\text{surface}) \rightarrow M_{N-1} + M$$

Table: surface cohesive energy of different tubes and the shift in the electrochemical dissolution potential relative to Pt(111)

reaction	$M_N(\text{tube}) \rightarrow M_{N-1} + M$	
	$\Delta E/eV$	$\Delta U_{ccw}/V$
Pt(111)	6.55	0.00
(6,3)	4.11	-1.22
(6,4)	5.17	-0.70
(6,6)	5.20	-0.68
(12,6)	5.53	-0.51
(12,8)	5.52	-0.52
(12,12)	6.05	-0.25
(13,13)	6.29	-0.13
(6,6)@(13,13)	5.98	-0.27

Figure. Surface cohesive energy of atoms in (13,13) tube

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Stability of the surfaces

Estimate of the shift in the electrochemical dissolution potential
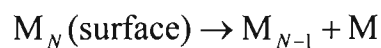
$$M_N(\text{surface}) \rightarrow M_{N-1} + M$$

Table: surface cohesive energy of different tubes and the shift in the electrochemical dissolution potential relative to Pt(111)

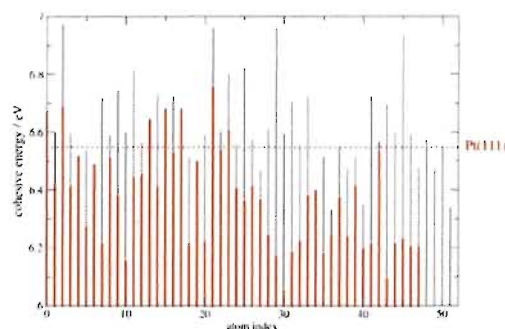| reaction	$M_N(\text{tube}) \rightarrow M_{N-1} + M$	
	$\Delta E/eV$	$\Delta U_{corr}/V$
Pt(111)	6.55	0.00
(6,3)	4.11	-1.22
(6,4)	5.17	-0.70
(6,6)	5.20	-0.68
(12,6)	5.53	-0.51
(12,8)	5.52	-0.52
(12,12)	6.05	-0.25
(13,13)	6.29	-0.13
(6,6)@(13,13)	5.98	-0.27

Figure. Surface cohesive energy of atoms in (12,12) tube
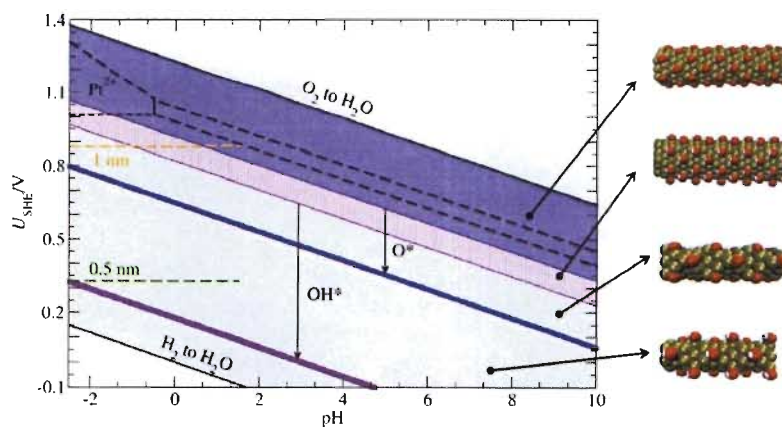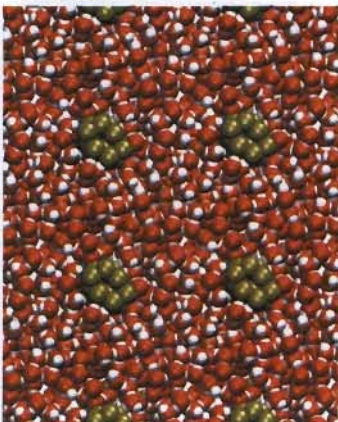
Pourbaix diagrams

Figure: Calculated surface Pourbaix diagrams for Pt nanotubes compared to a bulk Pourbaix diagrams (black dashed lines)
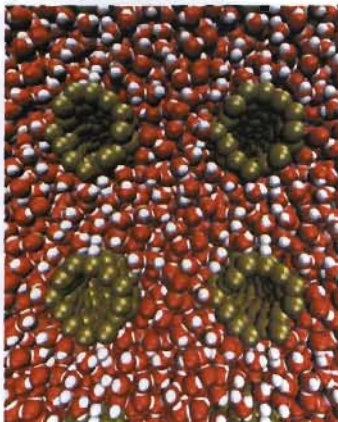
Pt nanotubes – ab initio MD simulations in water

Aim (1) characterize change of atomic and electronic structure on solvation
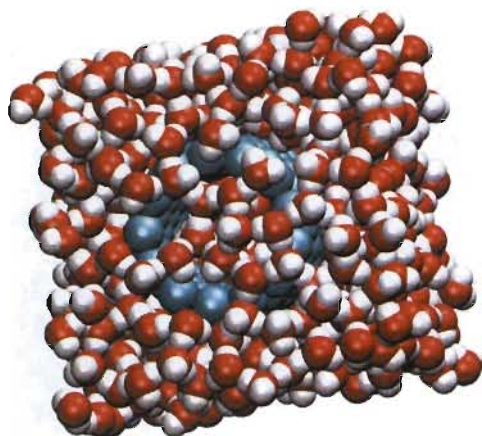(2) structure of water around curved surfaces - water-surface interface models

(6,6) and   **(13,13) SWPtNT in water**

~800 atom cell, 1300 MD steps
in 24h, 480 processors, average
~1min/step

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Pt nanotubes – ab initio MD simulations in water

20 Å length tube, d=10.9 Å in a 30 Å length
simulation box

bigger tubes accommodate water and ORR
intermediates

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Conclusions

- smaller nanotubes (~0.5 nm) bind oxygen/hydroxyl more strongly than Pt(111)

  larger nanotubes (~1 nm) bind oxygen/hydroxyl comparable or weaker than Pt(111)

  reduced ORR overpotential – SWPtNT with a diameter > 1nm

- control size/chirality – fine tuning of reactivity $\rightarrow$ separation of metal nanotubes by geometric specification or size

- all studied nanotubes more susceptible to electrochemical dissolution than Pt(111) – potential corrosion problem

Acknowledgements

Thank you for you attention

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Neil Henson & Fernando Garzon
C. Taylor, J. Rossmeisl, P. Lazic