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Density Functional Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanowires

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Physics and Chemistry of Materials

Los Alamos National Laboratory, Los Alamos, USA

metal nanotubes

- magic “structure” and conductance - nanoelectronics
- Au, Ag, Pt nanotubes less than 2nm thickness have been synthesized by an electron-beam technique in an UHV-TEM

Kondo et al. Science, 289, 606

metal nanotubes

- 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)

metal nanotubes

Pt nanotubes – electrocatalysis

NANO LETTERS

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Size-Dependent Enhancement of Electrocatalytic Performance in Relatively Defect-Free, Processed Ultrathin Platinum Nanowires

Christopher Koenigsmann,[†] Wei-ping Zhou,[†] Radoslav R. Adzic,[†] Eli Sutter,[§] and Stanislaus S. Wong^{*,†,||}

ABSTRACT We report on the synthesis, characterization, and electrocatalytic performance of ultrathin Pt nanowires with a diameter of less than 2 nm. An acid-wash protocol was employed in order to yield highly exfoliated, crystalline nanowires with a diameter of 1.3 ± 0.4 nm. The electrocatalytic activity of these nanowires toward the oxygen reduction reaction was studied in relation to the activity of both supported and unsupported Pt nanoparticles as well as with previously synthesized Pt nanotubes. Our ultrathin, acid-treated, unsupported nanowires displayed an electrochemical surface area activity of 1.45 mA/cm^2 , which was nearly 4 times greater than that of analogous, unsupported platinum nanotubes and 7 times greater than that of commercial supported platinum nanoparticles.

KEYWORDS Platinum, nanowires, electrocatalysis, oxygen reduction reaction

VIP Oxygen-Reduction Catalysts

DOI: 10.1002/anie.200700894

Supportless Pt and PtPd Nanotubes as Electrocatalysts for Oxygen-Reduction Reactions**

Zhongwei Chen, Mahesh Waje, Wenzhen Li, and Yushan Yan*

Angewandte
Chemie

Pt nanotubes

PtNT: Rolling-up Pt(111) sheet to form a tube

Roll-up
→

rolling vector: $R = na + mb$

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

$$a_c = 3.70 - 3.85 \text{ \AA}$$

Methodology

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

Free gibbs energy of the reactions

$$\begin{aligned}
 \Delta G_{\text{w,water}} &= \Delta E_{\text{w,water}} + \Delta \text{ZPE} + T\Delta S \\
 \Delta G(U, \text{pH}, T = 298\text{K}) &= \Delta G_{\text{w,water}} \underbrace{- eU}_{\text{bias effect}} + \underbrace{kT \ln(10) \text{pH}}_{\text{correction for the free energy of H}^+}
 \end{aligned}$$

Technical details

- VASP program
- DFT with PAW method using GGA approximation with PW91 exchange-correlation term
- 23 Å x 23 Å x nL cell, vacuum space twice the tubes diameter
- (1 x 1 x 4) – (1 x 1 x 21) k-point Monkhorst-Pack mesh
- plane-wave basis with a cutoff energy of 400 eV
- Methfessel-Paxton smearing of order 2 with sigma value of 0.2 eV

UNCLASSIFIED

Pt nanotubes

Pt nanowires

(6,6) NT

(13,13) NT

(6,6) NW

(6,6)@(13,13) NT

(6,6)@(13,13) NW

Pt nanotubes & nanowires: density of states

- electronic states distributed continuously from -7 eV all the way up, much smaller above 1 eV
- compared to DOS of Pt, many conspicuous peaks
- enables us to calculate the position of the *d*-band center – *d*-band theory

Pt nanotubes & nanowires: band structure

- number of electronic bands that cross Fermi level (conduction channels) quantized – conductance quantized
- position of Fermi level pushed up, number of conduction channels increases as the number of rows in NT increase

Pt nanotubes & nanowires: ORR

system	oxygen (fcc site)			hydroxyl (atop site)			hydroperoxyl (T-T* and atop)	
	0.25 ML	0.33 ML	0.5 ML	0.25 ML	0.33 ML	0.5 ML	0.25 ML	0.33 ML
	E_{ad}/eV	E_{ad}/eV	E_{ad}/eV	E_{ad}/eV	E_{ad}/eV	E_{ad}/eV	E_{ad}/eV	E_{ad}/eV
Pt	-4.42	-4.25	-4.07	-2.88	-2.92	-3.09	-1.24*/-1.15	-1.27*/-1.20
~ 0.5 nm								
(6,6)NT	-4.72	-4.41	-4.46	-3.54	-3.53	-3.52	-1.83	-1.78
(6,6)NW	-4.62	-4.38	-4.33	-3.30	-3.42	-3.36	-1.75	-1.69
~ 1.0 nm								
(13,13)NT	-4.14	-3.90	-3.92	-2.83	-2.87	-2.85	-1.28*/-1.42	-1.47
(6,6)@(13,13)NT	-4.05	-4.21	-4.06	-3.07	-3.13	-3.20	-1.24*/-1.38	-1.41
(6,6)@(13,13)NW	-4.04	-4.02	-3.97	-3.04	-3.10	-3.09	-1.30	-1.36

- hydroperoxyl dissociates on most of the adsorption sites – **4e⁻ ORR without peroxide formation preferred mechanism**

Pt nanotubes & nanowires: *d*-band theory

system	oxygen (fcc site)			d-band center
	0.25 ML E_{ad}/eV	0.33 ML E_{ad}/eV	0.5 ML E_{ad}/eV	
Pt	-4.42	-4.25	-4.07	-1.78 eV
~ 0.5 nm (6,6)NT	-4.72	-4.41	-4.46	-1.81 eV
(6,6)NW	-4.62	-4.38	-4.33	-1.75 eV
~ 1.0 nm (13,13)NT	-4.14	-3.90	-3.92	-2.00 eV
(6,6)@(13,13)NT	-4.05	-4.21	-4.06	-2.05 eV
(6,6)@(13,13)NW	-4.04	-4.02	-3.97	-2.13 eV

* T-T site dissociates

- no correlation between the shift in the *d*-band center relative to Fermi level and the oxygen adsorption energy
- adsorption of chemical species changes the local environment of the adsorption site (!)
- inadequacy of simple descriptors to predict reactivity

Pt nanotubes phase diagram

Dissociative oxygen reduction reaction (ORR) mechanism

hollow single-wall nanotubes and **non-hollow nanowires** with diameters **larger than 1nm** have smaller ORR overpotential than Pt(111) up to 100 meV

in agreement with experimental findings – *Nano Lett.* 2010, 19, 1806

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

Stability of the surfaces

Electrochemical dissolution can severely decrease the performance of the material

Estimate of the shift in the electrochemical dissolution potential based on the change in cohesive energy relative to Pt(111)

Stability of the surfaces

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

system	ΔE / eV	ΔU_{corr} / V
Pt	6.50	0.00
(6,6)NT	5.27	-0.62
(6,6)NW	5.54	-0.49
(13,13)NT	6.29	-0.11
(6,6)@(13,13)NT	5.50	-0.50
(6,6)@(13,13)NW	5.70	-0.40

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

Conclusions

- smaller nanotubes (~ 0.5 nm) bind oxygen/hydroxyl more strongly than Pt(111) - poisoning
- larger single-wall nanotubes and nanowires (~ 1 nm) bind oxygen/hydroxyl comparable or weaker than Pt(111) $\Rightarrow$ reduced ORR overpotential
- control size/chirality – fine tuning of reactivity $\rightarrow$ separation of metal nanotubes by geometric specification or size
- hydroperoxyl dissociates on most of the adsorption sites – **$4e^-$ ORR without peroxide formation preferred mechanism**
- all studied nanotubes more susceptible to electrochemical dissolution than Pt(111) – potential corrosion problem

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