Computational Design of Advanced Nanoalloy Materials

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Overview of My Previous RES Projects

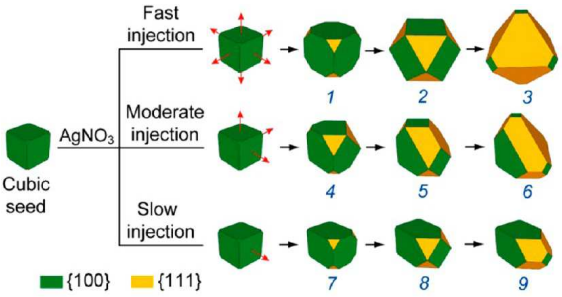
- QCM-2016-2-0020
  Structure and surface composition of Pt-based bimetallic nanoparticles for catalysis and beyond
- QCM-2015-3-0012, QCM-2016-1-0006
  Structure and surface composition of Ni-based bimetallic nanoparticles as catalysts
- QCM-2015-1-0025, QCM-2015-2-0016
  Determination of chemical ordering in large bimetallic particles from density-functional calculations
- QCM-2014-1-0012, QCM-2014-2-0024, QCM-2014-3-0015
  Towards more realistic modelling of industrially important Pd/CeO_2 and Pt/CeO_2 catalysts
- QCM-2012-2-0020, QCM-2012-3-0018, QCM-2013-1-0019, QCM-2013-2-0016
  Towards catalysts of new generation: Active sites of ionic Pt in nanostructured ceria
- QCM-2011-3-0012, QCM-2012-1-0006
  Computer modeling to gain an atomistic insight into the energy storage processes mediated by ceria
- QCM-2011-2-0019
  Mechanisms of olefins hydrogenation on nanostructured Pd catalysts: I. Effect of the olefin type
- QCM-2010-3-0004, QCM-2011-1-0029
  Reactivity Control in Catalysis by Nanostructuring: I. Modelling Platinum/Ceria Nanostructures

- Over 30 publications in referred journals 2011-2016 acknowledging RES support:
  Angew Chemie Int Ed – 2, *Chemical Science*, *Nature Materials* – 2

Manufacturing of Metal Nanoparticles

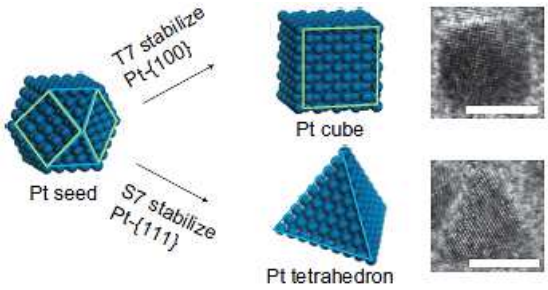
- Experimental size and shape control via preparation conditions

Growth of Ag cubic seeds in solutions controlled via thermodynamics *vs.* kinetics



Xia *et al*. *J Am Chem Soc* 137 (2015) 7947

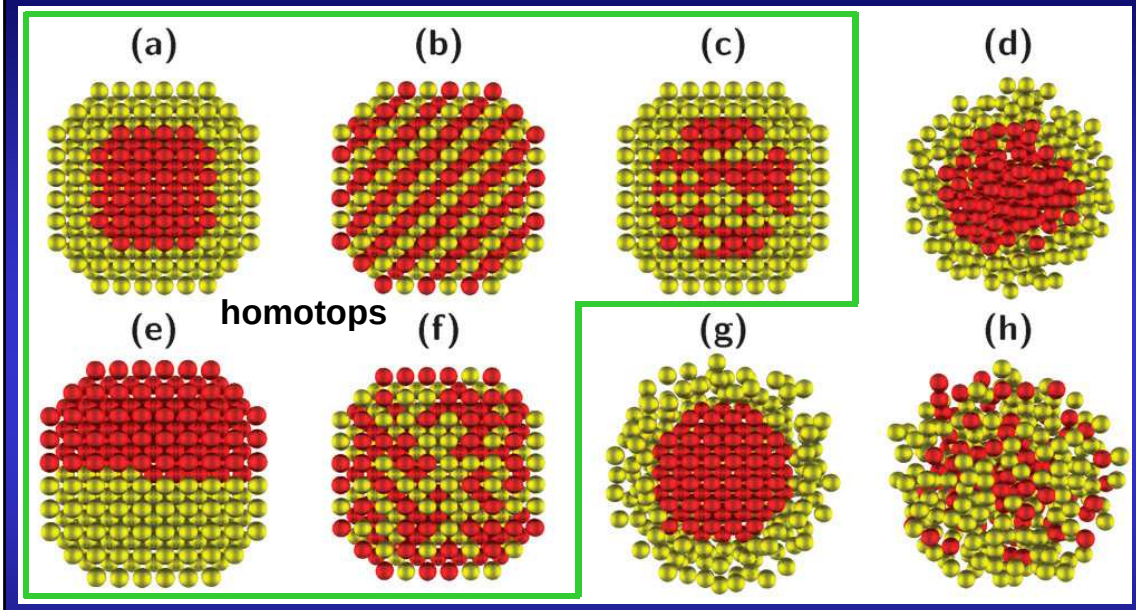
Pt nanocrystals selectively shaped using facet-specific peptide sequences



Chiu *et al*. *Nature Chem* 3 (2011) 393

- Heterometallic particles: greatly increased diversity of chemical and physical characteristics *vs*. those of monometallic particles
- Properties of bimetallic particles A_YB_{N-Y} additionally depend on
  - composition Y/N-Y ⇒ can be tuned experimentally
  - chemical ordering ⇒ positions of atoms A and B in a nanocrystallite

Archetypal Patterns Exhibited by Bimetallic Nanoalloys

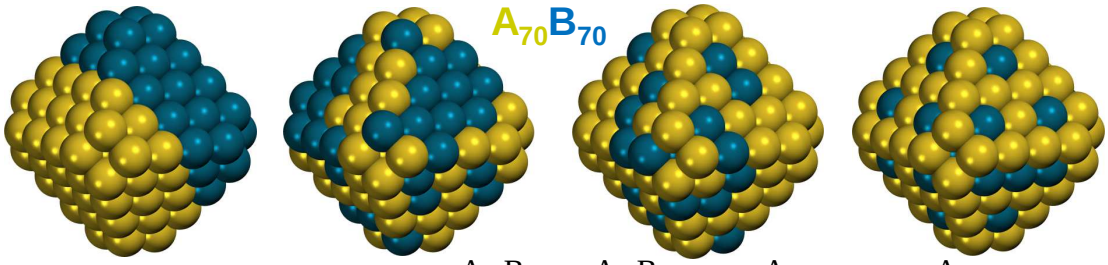


a core-shell, ***b*** ordered (intermetallics), ***c*** alloyed core-shell, ***d*** liquid core-shell
e Janus-like, ***f*** random, ***g*** solid core-liquid shell, ***h*** liquid

Calvo *Phys Chem Chem Phys* 17 (2015) 27922

Chemical (Atomic) Ordering in Bimetallic Nanoparticles

Homotops of a bimetallic particle



$$E_{\mathrm{DFT}} \approx E_{\mathrm{TOP}} = E_0 + \varepsilon^{\mathrm{A-B}}_{\mathrm{BOND}} N^{\mathrm{A-B}}_{\mathrm{BOND}} + \varepsilon^{\mathrm{A}}_{\mathrm{CORNER}} N^{\mathrm{A}}_{\mathrm{CORNER}} + \varepsilon^{\mathrm{A}}_{\mathrm{EDGE}} N^{\mathrm{A}}_{\mathrm{EDGE}} + \varepsilon^{\mathrm{A}}_{\mathrm{TERRACE}} N^{\mathrm{A}}_{\mathrm{TERRACE}}$$

- Lowest-energy atomic positions A/B in a lattice A_YB_{N-Y} ($N \geq 80$)?
  – huge number of homotops ~2^N for $A_{N/2}B_{N/2}$, i.e. >10^{24} for N = 80
- Pre-screening of homotops using accurate energies computed very fast
- Topological energy expressions E_{TOP} defined by E_{DFT} energies of 20-30 bimetallic nanocrystallites with ~100-200 atoms

Kozlov, Kovács, Ferrando, Neyman How to determine accurate chemical ordering in several nanometer large bimetallic crystallites from electronic structure calculations *Chemical Science* 6 (2015) 3868

Optimization Using Topological Expressions $E_{TOP}(\varepsilon_i,N_i)$

DFT energies of trial homotops; descriptors ε_i

↓ $E_{DFT} \approx E_{TOP}(\varepsilon_i,N_i)$

Monte-Carlo optimization of homotops (~ 10^6 steps) ← New ε_i (Re-fit ε_i with new homotops)

↓ Lowest-energy homotops

DFT geometry optimization

↓ E_{DFT}

Analysis → Poor agreement $E_{DFT} \leftrightarrow E_{TOP}$

↓ Agreement $E_{DFT} \leftrightarrow E_{TOP}$

Enjoy Success

Accuracy ΔE
energy difference of the lowest-energy DFT and TOP homotops

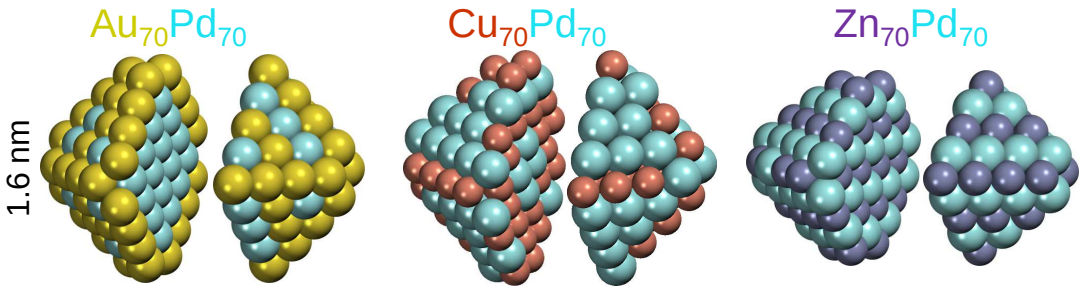
Precision δ
twice the standard deviation between E_{DFT} and E_{TOP} for ≥10 homotops not in the fitting set

< 50 DFT calculations enough to find the lowest-energy homotop

- **MC optimization is just a pre-screening**

⇒ resulting homotops computed via DFT

Optimized Ordering of Atoms in Bimetallic Nanoparticles



$$E_{\mathrm{TOP}}[\mathrm{Au_{70}Pd_{70}, meV}] = E_0 - 13N_{\mathrm{Pd-Au}} - 404N^{\mathrm{Au}}_{\mathrm{CORNER}} - 301N^{\mathrm{Au}}_{\mathrm{EDGE}} - 200N^{\mathrm{Au}}_{\mathrm{TERRACE}}$$

$$\Delta E = 26\ \mathrm{meV}$$

$$E_{\mathrm{TOP}}[\mathrm{Cu_{70}Pd_{70}, meV}] = E_0 - 26N_{\mathrm{Pd-Cu}} + 95N^{\mathrm{Cu}}_{\mathrm{CORNER}} + 147N^{\mathrm{Cu}}_{\mathrm{EDGE}} + 183N^{\mathrm{Cu}}_{\mathrm{TERRACE}}$$

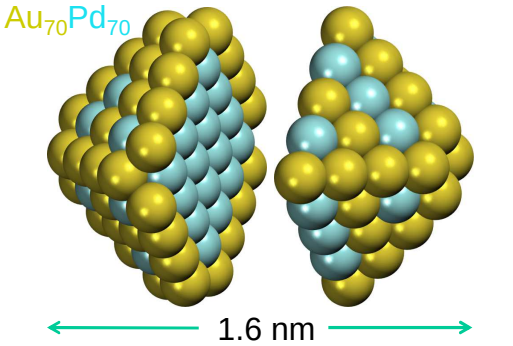
$$\Delta E = 121\ \mathrm{meV}$$

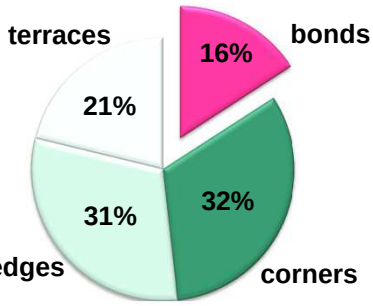
$$E_{\mathrm{TOP}}[\mathrm{Zn_{70}Pd_{70}, meV}] = E_0 - 160N_{\mathrm{Pd-Zn}} - 251N^{\mathrm{Zn}}_{\mathrm{CORNER}} - 205N^{\mathrm{Zn}}_{\mathrm{EDGE}} - 90N^{\mathrm{Zn}}_{\mathrm{TERRACE}} - 105N_{\mathrm{LAYER}}$$

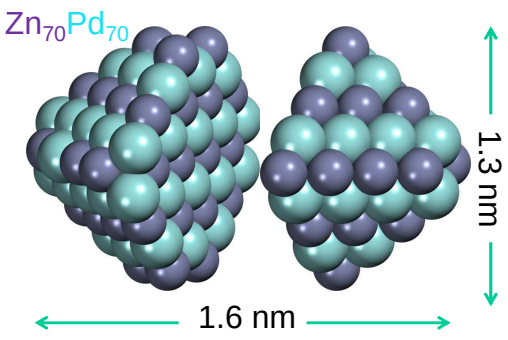
$$\Delta E = 0\ \mathrm{meV}$$

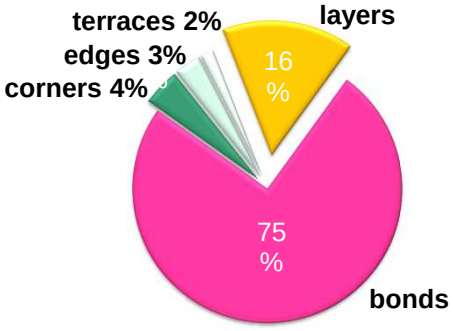
Kozlov, Kovács, Ferrando, Neyman *Chemical Science* 6 (2015) 3868

Energy Contributions to Nanoalloy Formation







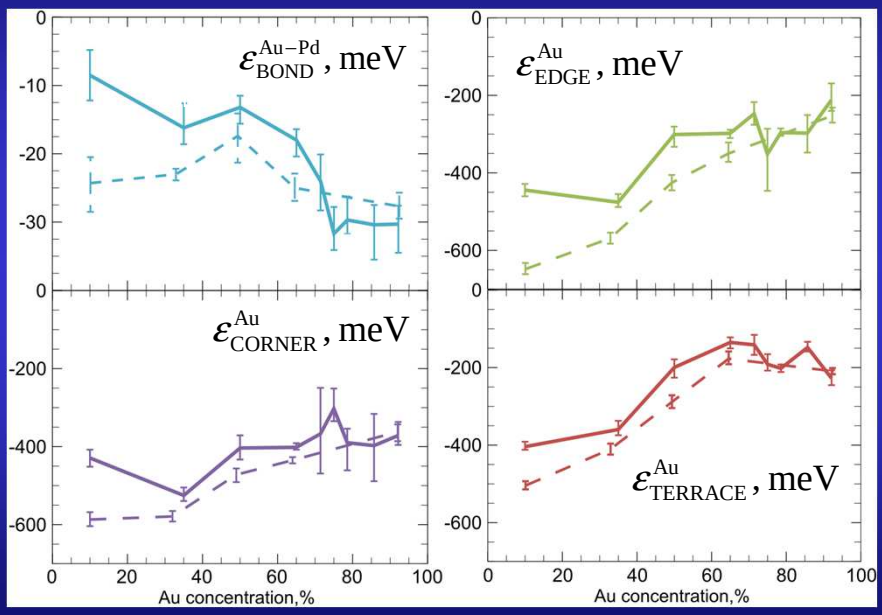


Kozlov, Kovács, Ferrando, Neyman *Chemical Science* 6 (2015) 3868

Particle Size Effect on the Descriptors: Transferability

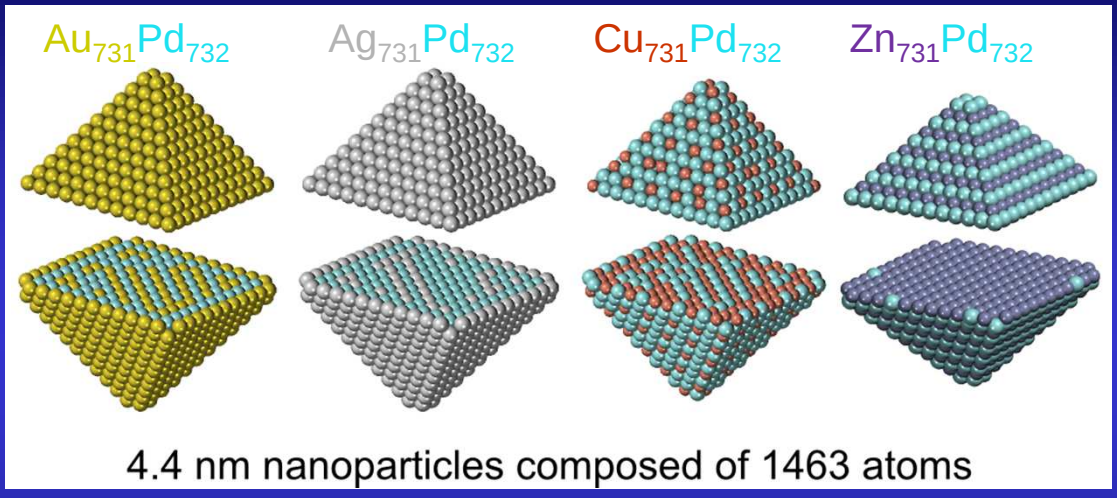
$$E_{TOP}(Au-Pd) = E_0 + \varepsilon^{Au-Pd}_{BOND} N^{Au-Pd}_{BOND} + \varepsilon^{Au}_{CORNER} N^{Au}_{CORNER} + \varepsilon^{Au}_{EDGE} N^{Au}_{EDGE} + \varepsilon^{Au}_{TERRACE} N^{Au}_{TERRACE}$$

1.6 nm $Au_{140-Y}Pd_Y$ particle – – – 1.2 nm $Au_{79-Y}Pd_Y$ particle



- Limited dependence of descriptors on the NPs size at a given composition

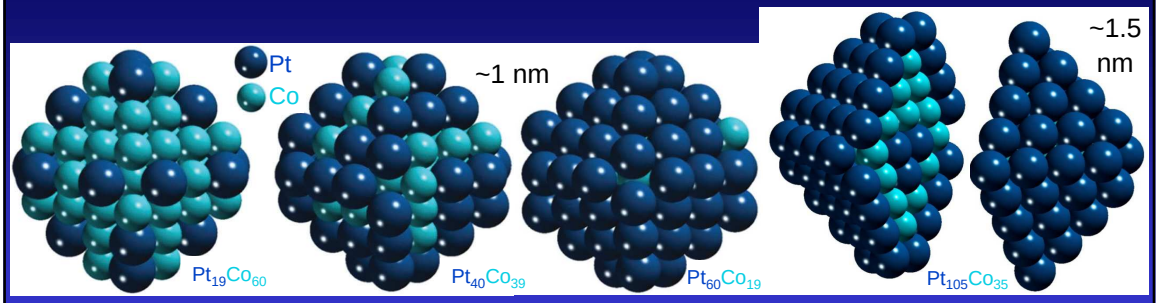
DFT-Based Optimized Chemical Ordering in Nanoalloys



- Descriptors only weakly depend on the NP size for a given composition
  ⇒ descriptors determined from DFT energies for NPs of 10^2 atoms allow us accurately assess chemical ordering in NPs of 10^3 (10^4) atoms

Kozlov, Kovács, Ferrando, Neyman *Chem Sci* 6 (2015) 3868

Case Study I: Chemical Ordering in Pt-Co Nanoparticles

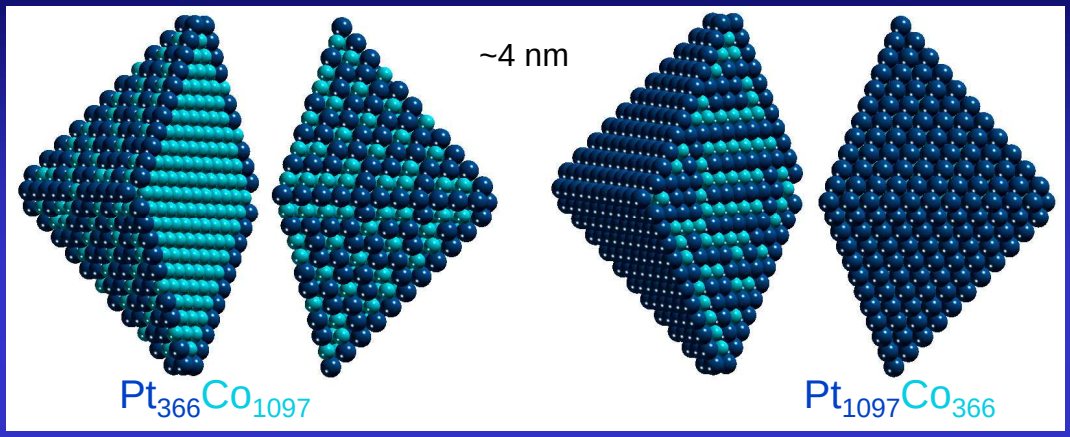


meV	NPs	$\varepsilon^{Pt}_{corner}$	ε^{Pt}_{edge}	$\varepsilon^{Pt}_{terrace}$	$\varepsilon^{Pt-Co}_{bond}$	ΔE	$\delta(E_{DFT} - E_{TOP})$
$Pt_{19}Co_{60}$	23	-1309	-1230	-918	-67	48	118
$Pt_{40}Co_{39}$	46	-436	-884	-327	-30	89	150
$Pt_{60}Co_{19}$	52	-596	-714	-525	-35	95	154
$Pt_{105}Co_{35}$	35	-667	-733	-464	-45	74	155

- Pt_YCo_{1-Y}-core@Co-rich-subsurface@Pt-rich-shell structure

Kovács, Kozlov, Matolínová, Vorokhta, Matolín, Neyman Revealing chemical ordering in Pt–Co nanoparticles using electronic structure calculations and X-ray photoelectron spectroscopy *Phys Chem Chem Phys* 17 (2015) 28298

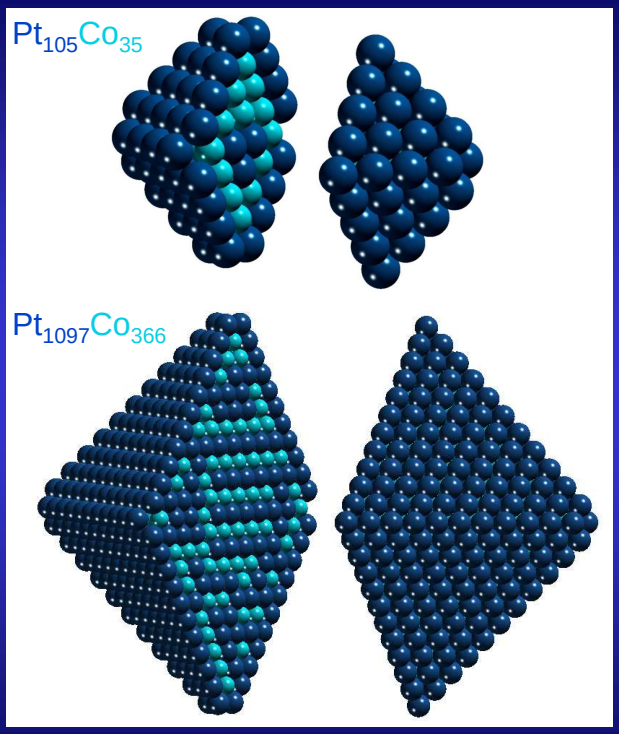
Larger Pt-Co Nanoparticles

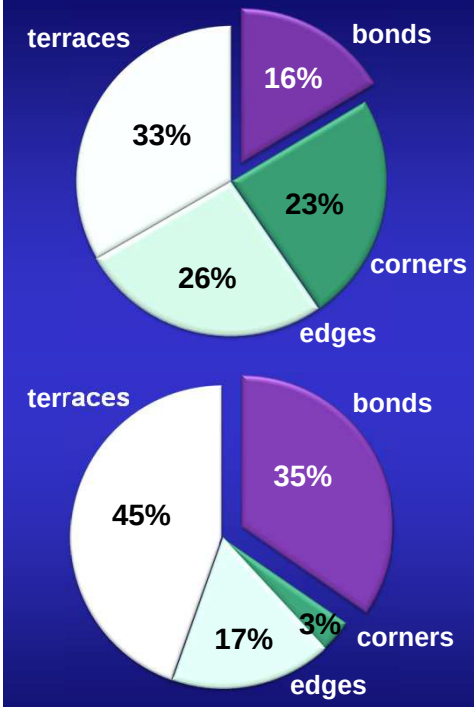


- Descriptors ε_i calculated for Pt_YCo_{79-Y} and Pt_YCo_{140-y} only weakly depend on the particle size for each composition
- Optimized chemical ordering in Pt_YCo_{1463-Y} nanoparticles
  $\Rightarrow$ *consistent with experimental results for PEM fuel cell cathode catalysts*

Kovács, Kozlov, Matolínová, Vorokhta, Matolín, Neyman *Phys Chem Chem Phys* 17 (2015) 28298

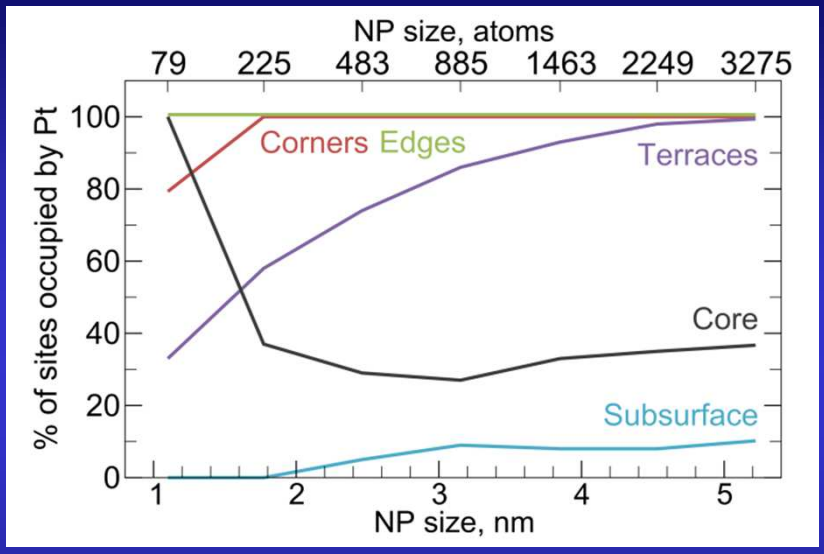
Binding Contributions of Nanostructuring *vs*. Bulk Effects





Kovács, Kozlov, Matolínová, Vorokhta, Matolín, Neyman *Phys Chem Chem Phys* 17 (2015) 28298

Pt Atoms in Various Sites of Growing 1:1 Pt-Co Particles

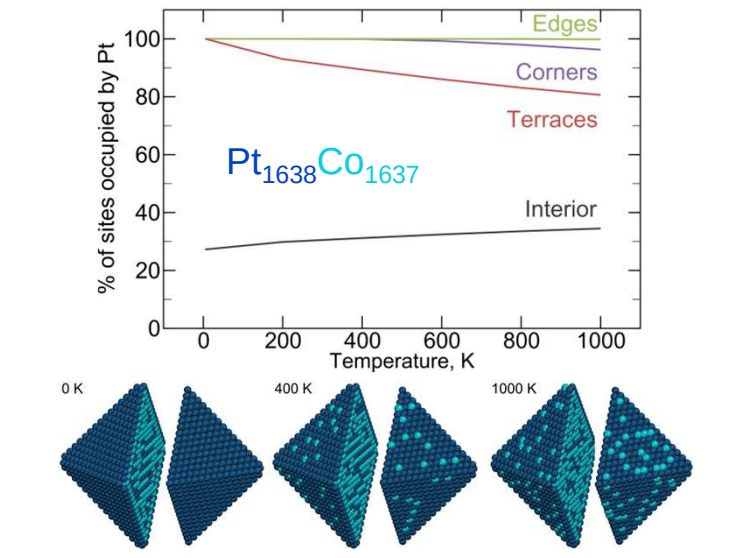


- Clear preference of Pt to occupy surface sites: edges > corners > terraces
- Core Pt concentration ~35% leaves not enough Pt to cover the surface

  ⇒ no complete outer Pt shell in particles <4.5 nm large (ca. 2300 atoms)

Kovács, Kozlov, Matolínová, Vorokhta, Matolín, Neyman *Phys Chem Chem Phys* 17 (2015) 28298

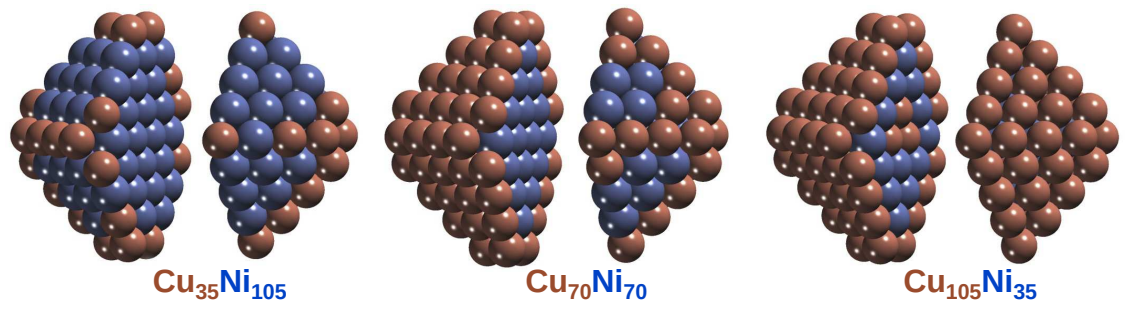
Ordering in $Pt_{1638}Co_{1637}$ NPs at Elevated Temperature



- Shortage of Pt atoms to form a full Pt-skin in 6 nm large $Pt_{1638}Co_{1637}$ NPs even at moderate temperatures is caused by Pt accumulation in the core
- More stable full Pt-skin in larger 1:1 NPs due to lower surface to bulk ratio

Vorokhta, Khalakhan, Václavů, Kovács, Kozlov, Kúš, Skála, Tsud, Lavková, Potin, Matolínová, Neyman, Matolín *Appl Surf Sci* 365 (2016) 245

Case Study II: Ordering of Atoms in Cu-Ni Nanoparticles

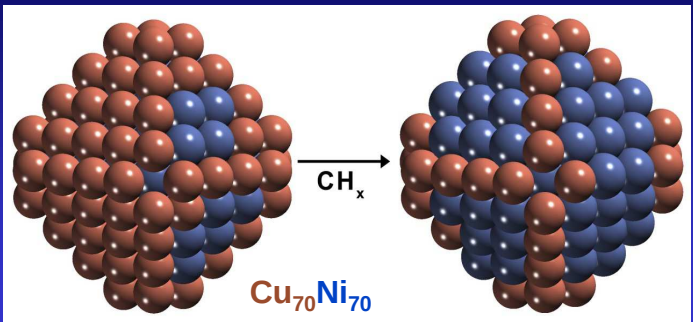


- Descriptors ε_i point to the surface segregation of Cu at all compositions; preference order: corner > edge > terrace
- Small positive / zero descriptors for Cu-Ni bond formation ⇒ no mixing

meV	NPs	$\varepsilon^{Cu}_{corner}$	ε^{Cu}_{edge}	$\varepsilon^{Cu}_{terrace}$	$\varepsilon^{Cu-Ni}_{bond}$	ΔE	$\delta(E_{DFT} - E_{TOP})$
$Cu_{35}Ni_{105}$	27	-413	-300	-193	8	32	104
$Cu_{70}Ni_{70}$	34	-362	-350	-127	11	28	92
$Cu_{105}Ni_{35}$	31	-460	-315	-198	0	46	88

Wolfbeisser, Kovács, Kozlov, Föttinger, Bernardi, Klötzer, Neyman, Rupprechter *Catal Today* (2016), doi: 10.1016/j.cattod.2016.04.022

Adsorbate-Induced Ni Surface Segregation in Cu-Ni NPs



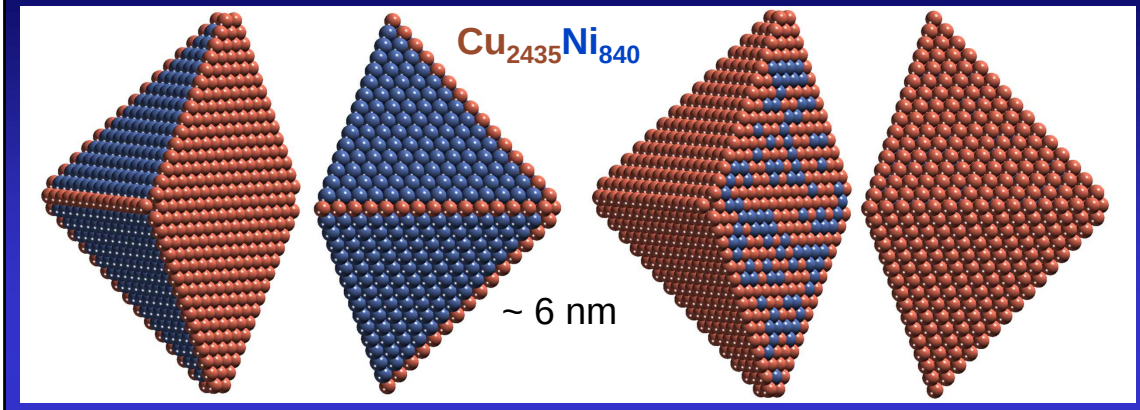
- Adsorption of CH_x preferred on hollow sites
- Stronger adsorption on Ni than on Cu sites drives Ni surface segregation
- CH_x adsorption energy difference on Ni_3 and Cu_3 sites increases in the order $CH_3 < CH_2 < CH < C$, from 0.5 eV (CH_3) to ca. 2.0 eV (C atom)

⇓

- Different adsorbed CH_x groups induce Ni segregation to a different extent

Wolfbeisser, Kovács, Kozlov, Föttinger, Bernardi, Klötzer, Neyman, Rupprechter
Catal Today (2016), doi: 10.1016/j.cattod.2016.04.022

Design of Optimal Catalysts Using Theoretical Results



- 'Ideal' catalyst: Ni in surface terrace sites and Cu in edge and bulk sites
- Lowest-energy homotop $Cu_{2435}Ni_{840}$ at 0 K with surface-segregated Cu

⇓

- Estimate from the descriptors and adsorption energies of CH_x groups surface coverage compatible with stabilizing optimal catalyst structure
  ⇒ exposing active surface Ni, resistant to coke formation

Wolfbeisser, Kovács, Kozlov, Föttinger, Bernardi, Klötzer, Neyman, Rupprechter
Catal Today (2016), doi: 10.1016/j.cattod.2016.04.022

Summary

- Accessible at the DFT level of accuracy chemical ordering in bimetallic crystallites of ~10^2 ÷ 10^4 atoms, at the sizes relevant to technical catalysis
  - NPs of ca. 80 ÷ 300 atoms ⇒ DFT optimizing the lowest-energy homotops pre-screened using topological energy equations defined by 4-5 descriptors of clear physical origin
  - NPs of ≤10^4 atoms, which are too large for DFT calculations ⇒ optimizing by the accurate topological energy equations
- Descriptor values in the topological energy equations rationalize the stability of particular homotops and characterize the binding
- The method allows to greatly facilitate the knowledge-driven design and manufacturing of nanoalloys with tailored properties

Ilker Demiroglu, Albert Bruix, KN, Hristiyan Aleksandrov
Alberto Figueroba, Sergey Kozlov, Gábor Kovács 02/2014

MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

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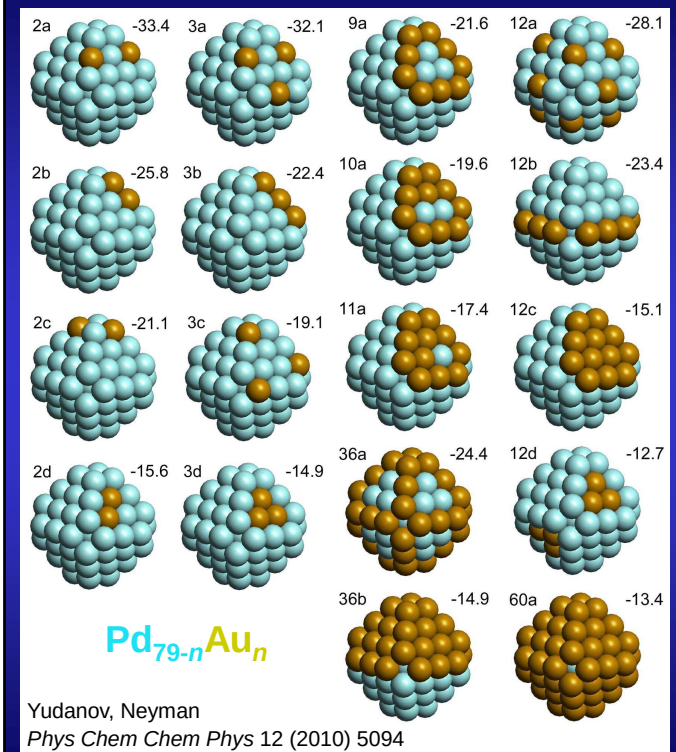
- European Commission FP7 grant Nº310191
  Design of thin-film nanocatalysts for on-chip fuel cell technology
- COST CM1104 *Reducible oxide chemistry, structure and functions*
- Red Española de Supercomputación

Recent Publications on Nanoalloys with RES Support

- Neitzel, Kovács, Lykhach, Tsud, Kozlov, Skála, Vorokhta, Matolín, Neyman, Libuda. Steering the formation of supported Pt–Sn nanoalloys by reactive metal-oxide interaction. *RSC Adv* 6 (2016) 85688
- Neitzel, Kovács, Lykhach, Kozlov, Tsud, Skála, Vorokhta, Matolín, Neyman, Libuda. Atomic ordering and Sn segregation in Pt-Sn nanoalloys supported on CeO_2 thin films. *Top Catal* (2016), doi: 10.1007/s11244-016-0709-5
- Wolfbeisser, Kovács, Kozlov, Föttinger, Bernardi, Klötzer, Neyman, Rupprechter. Surface composition changes of CuNi-ZrO_2 catalysts during methane decomposition: An operando NAP-XPS and density functional study. *Catal Today* (2016), doi: 10.1016/j.cattod.2016.04.022
- Vorokhta, Khalakhan, Václavů, Kovács, Kozlov, Kúš, Skála, Tsud, Lavková, Potin, Matolínová, Neyman, Matolín. Surface composition of magnetron sputtered Pt-Co thin film catalyst for proton exchange membrane fuel cells. *Appl Surf Sci* 365 (2016) 245
- Kovács, Kozlov, Matolínová, Vorokhta, Matolín, Neyman. Revealing chemical ordering in Pt-Co nanoparticles using electronic structure calculations and X-ray photoelectron spectroscopy. *Phys Chem Chem Phys* 17 (2015) 28298
- Kozlov, Kovács, Ferrando, Neyman. How to determine accurate chemical ordering in several nanometer large bimetallic crystallites from electronic structure calculations. *Chemical Science* 6 (2015) 3868

Stability of Nanoparticles $Pd_{79-n}Au_n$ (n= 2÷60)



Yudanov, Neyman
Phys Chem Chem Phys 12 (2010) 5094

- Excess of the total energy $E(Pd_{79-n}Au_n)$ *vs*. $E(Pd_{79})$ and $E(Au_{79})$, per n [kJ/mol]
- Energetically unfavored Au atom inside NP
- Au atoms on edges are more stable than inside {111} facets

Problems of a restricted search

- Applicable only for "impurities"
- Unsystematic
- Easy to miss lowest-energy (ground state) configurations