Multi-Scale Simulations of the Growth and Assembly of Colloidal Nanoscale Materials

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Complex Nanostructures in Colloidal Crystal Growth: How Do They Form?

- Ostwald Ripening
- Cluster-Cluster Aggregation
- Oriented Attachment
- How Does OA Happen?
Complex Nanostructures in Colloidal Crystal Growth: Oriented Attachment

Oriented Attachment of TiO$_2$: Intrinsic Crystal Forces

Oriented Attachment and the Mesocrystal State: The Role of Solvent


Complex Nanostructures in Colloidal Crystal Growth: Capping Agents

“One-Pot” Solution-Phase Synthesis of Nanostructured Metal Materials

Polyol Process

Solvent: Ethylene Glycol
Salt: AgNO₃
“Stabilizer”: PVP

Heat at ~400 K

N,N-DMF Reduction

Solvent: N,N-DMF
Salt: AgNO₃
“Stabilizer”: PVP

All Kinds of Nano-Shapes

What Happens in the Pot?

Nanostructure Formation: General Aspects


Reduction of Ag

Nucleation

Seed Formation

Growth

Determined by Salt and... Solvent or PVP?

Probably Determined by PVP...
Does PVP Prefer Ag(100) Over Ag(111)?

Nanowires from Multiply-Twinned Decahedral Seeds

Nanocubes from Single-Crystal Cubo-Octahedral Seeds


Interaction of PVP with Ag(100) and Ag(111): First-Principles Challenges

Historically DFT Described Direct Bonds, Including vdW Interactions is New...

Interaction of PVP with Ag(100) and Ag(111): VASP 5.2.11

- (4×4×14) Super Cell
  - Slab: 6 layers
  - Vacuum: 8 layers
- PAW-PBE (GGA) ± DFT-D2 ± TS*
  - Assess the Influence of vdW Interactions
- Cut-off: 29.4 Ry
- \( k \)-points: (4×4×1)
- Ab-initio Molecular Dynamics
- Static Total-Energy Calculations

*Implemented in VASP by Wissam Al-Saidi
van der Waals Interactions in DFT: How Do We Describe Ag??

\[
E_{vdW} = -\sum_{A,B} \frac{f_{damp} C_{6AB}}{R_{AB}^{6}} + f_{damp}(R_{AB}, R_{AB}^{0}) = \frac{1}{1 + \exp[-d(f(R_{AB}) - 1)]}
\]

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>DFT-D2\textsuperscript{a}</th>
<th>TS+ZK\textsuperscript{b+c}</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{6}) (J nm(^6) mol(^{-1}))</td>
<td>---</td>
<td>24.67</td>
<td>6.89</td>
<td>6.25\textsuperscript{d}</td>
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<tr>
<td>(R^{0}(\text{Å}))</td>
<td>---</td>
<td>1.64</td>
<td>1.34</td>
<td>---</td>
</tr>
<tr>
<td>(a_{Ag}(\text{Å}))</td>
<td>4.16</td>
<td>4.15</td>
<td>4.02</td>
<td>4.07\textsuperscript{e}</td>
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<tr>
<td>(\Delta_{12} \text{Ag(100)}(%))</td>
<td>-2.05</td>
<td>1.3</td>
<td>-1.75</td>
<td>±1.5\textsuperscript{f,g}</td>
</tr>
<tr>
<td>(\Delta_{12} \text{Ag(111)}(%))</td>
<td>-0.3</td>
<td>1.61</td>
<td>-0.32</td>
<td>0.5 ± 0.8\textsuperscript{h}</td>
</tr>
</tbody>
</table>

\textsuperscript{g}F. R. De Boer, \textit{et al.}, Cohesion in Metals, Amsterdam, (1988).
Binding Conformations: No vdW Interactions

Experimental IR and XPS: PVP Binds to Ag via the O and/or N Atom.

Binding Energies: No vdw Interactions

\[ E_{bind} = -(E_{molecule+surface} - E_{molecule} - E_{surface}) \]

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>Ethane</th>
<th>2-Pyrrolidone</th>
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</thead>
<tbody>
<tr>
<td>(100) Hollow</td>
<td>0.0</td>
<td>0.19</td>
</tr>
<tr>
<td>(100) Bridge</td>
<td>0.0</td>
<td>0.22</td>
</tr>
<tr>
<td>(100) Top</td>
<td>-</td>
<td>0.21</td>
</tr>
<tr>
<td>(111) fcc Hollow</td>
<td>0.0</td>
<td>0.19</td>
</tr>
<tr>
<td>(111) hcp Hollow</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>(111) Bridge</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>(111) Top</td>
<td>-</td>
<td><strong>0.26</strong></td>
</tr>
</tbody>
</table>


**Ag(100)**

Ag(111)

Preference for Ag(111): Contrary to Expectations

Predominantly vdw
vdW Interactions Support Structure-Directing Hypothesis

\[ E_{\text{bind}} = -(E_{\text{molecule+surface}} - E_{\text{molecule}} - E_{\text{surface}}) \]

<table>
<thead>
<tr>
<th>Site</th>
<th>PBE</th>
<th>PBE DFT-D2</th>
<th>PBE TS+ZK</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) Hollow</td>
<td>0.19</td>
<td>1.05</td>
<td>0.59</td>
</tr>
<tr>
<td>(100) Bridge</td>
<td>0.22</td>
<td>1.34</td>
<td>0.77</td>
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<tr>
<td>(100) Top</td>
<td>0.21</td>
<td>1.05</td>
<td>0.60</td>
</tr>
<tr>
<td>(111) fcc</td>
<td>0.19</td>
<td>0.61</td>
<td>0.58</td>
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<td>(111) hcp</td>
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<td>0.80</td>
<td>0.58</td>
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<tr>
<td>(111) Bridge</td>
<td>0.20</td>
<td>0.70</td>
<td>0.62</td>
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<tr>
<td>(111) Top</td>
<td>0.26</td>
<td>0.79</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Why Such Big Differences Between Methods??
DFT-D2: Ag(100) Reconstructs

Ag(100) Reconstruction has not been Observed Experimentally...

\[ \Delta E_{\text{hex}} = E_{\text{hex}} - E_{(100)} = -0.27 \text{ eV} \]
TS+ZK:2-Pyrrolidone on Ag(100)

Lots of Options!
Binding via O and N

PVP $\sim 139$ Times More Likely to Bind to Ag(100) “Sides” than Ag(111) “Ends”

$$\frac{P_{(100)}}{P_{(111)}} = 139 \approx \exp(\Delta E / kT); \quad T = 400K$$
TS+ZK Method: Break-Down of Binding Energy

\[ E_{bind} = E_{vdW} + E_{Pauli} + E_{directbond} \]

<table>
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<tr>
<th>Site</th>
<th>TS+ZK Energies</th>
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<tr>
<td></td>
<td>TS+ZK Geometries</td>
</tr>
<tr>
<td>(100) Hollow</td>
<td></td>
</tr>
<tr>
<td>(100) Bridge</td>
<td></td>
</tr>
<tr>
<td>(100) Top</td>
<td></td>
</tr>
<tr>
<td>(111) Top (\perp)</td>
<td>0.64</td>
</tr>
<tr>
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### TS+ZK Method: Break-Down of Binding Energy

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E_{\text{bind}} = E_{\text{vdW}} + E_{\text{Pauli}} + E_{\text{direct bond}}
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<th>PBE Energies</th>
<th>(\Delta)</th>
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<tr>
<td></td>
<td>TS+ZK Geometries</td>
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<td>E_{vdW}</td>
</tr>
<tr>
<td>(100) Hollow</td>
<td></td>
<td></td>
<td>0.78</td>
</tr>
<tr>
<td>(100) Bridge</td>
<td></td>
<td></td>
<td>0.81</td>
</tr>
<tr>
<td>(100) Top</td>
<td></td>
<td></td>
<td>0.77</td>
</tr>
<tr>
<td>(111) Top ⊥</td>
<td></td>
<td>0.64</td>
<td>0.12</td>
</tr>
<tr>
<td>(111) Bridge ⊥</td>
<td></td>
<td>0.62</td>
<td>0.09</td>
</tr>
<tr>
<td>(111) Bridge</td>
<td></td>
<td></td>
<td>0.63</td>
</tr>
</tbody>
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Ag(100): vdW and Direct Bonding Synergize
### TS+ZK Method: Break-Down of Binding Energy

\[ E_{\text{bind}} = E_{\text{vdW}} + E_{\text{Pauli}} + E_{\text{direct bond}} \]

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<th>Site</th>
<th>TS+ZK Energies</th>
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<th>Δ</th>
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<td>(111) Bridge</td>
<td></td>
<td></td>
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**Ag(111):** vdW is the Dominant Attractive Force

Sometimes the **only** Attractive Force
Conclusions

• We Studied Surface-Sensitivity of PVP Binding to Ag(111) and Ag(100)

• We Observed Stronger Binding to Ag(100) when we Include vdw As Inferred by Experiment

• DFT-D2 Reconstructs Ag(100) 😞

• Ag(100) Preference from Synergy Between vdw Attraction and Direct Bonding
Oriented Attachment in Crystal Growth: Role of Intrinsic Crystal Forces

See Also:

HRTEM: Oriented Attachment of TiO$_2$ Nanoparticles
Dipole-Dipole Interactions May Assemble Nanoparticles


CdTe Nanoparticle Chains
TiO$_2$ (Anatase) Nanocrystals

\[ U(rij) = A_{ij} \exp \left( -\frac{rij}{\rho_{ij}} \right) - \frac{C_{ij}}{rij^6} + \frac{q_i q_j}{rij} \]

\[ \mu = \sum_i q_i r_i \]

\( \mu = 0 \)
\( \mu = 35 \text{ D} \)
\( \mu = 75 \text{ D} \)
\( \mu = 250 \text{ D} \)

Two Wulff Nanocrystals

(001) Truncated Nanocrystals

(112) Truncated Nanocrystals

Matsui-Akaogi Force Field
Mol. Sim. 6, 239, 1991.

*
Aggregation of Wulff Nanocrystals
Nanocrystal Aggregation: The Hinge Mechanism

Initial Contact of Edges: The “Hinge”

Rotation About the “Hinge”
Nanocystal Aggregation: Driven by Electrostatic Forces

Nanocrystal Aggregation: Driven by Multipoles from Under-Coordinated Surface Atoms

Simulation vs. Experiment: Still Have a Way to Go

HRTEM Image Showing Oriented Attachment of 5 TiO$_2$ Nanoparticles

Aqueous Environment Hour (or longer) Times

Vacuum Environment Nanosecond Times
Nanocrystal Aggregation is Driven by Local Interactions.

We Should Re-Think the Dipole Idea...


*Also found this for capped and uncapped PbSe...*
1D Nanostructures form via Mesocrystals and Oriented Attachment

**Goethite Nanowires**


**Ag Nanowires**

Solvent Ordering and Solvation Forces

Solvent ordering around solvophilic nanoparticles


Solvent Density Profile
MD: Aggregation of a Small, Isotropic* Crystal with a Larger, Anisotropic Crystal

*Relatively Rectangular Cuboid
*Relatively Square Plate

- Generic Anisotropic fcc Nanoparticles
- Solvophilic Nanoparticles
- Strong vdW Attraction (Ag)
- Isotropcic Organic Solvent
Aggregation of Small and Large Nanocrystals: Mesocrystal States

Mesocrystal State 1
One Solvent Layer

Mesocrystal State 2
Two Solvent Layers
Aggregation of Small and Large Nanocrystals: Mesocrystal States

**Mesocrystal States: Free-Energy Minima**

Escape-Time Distribution

\[ f(t) = R e^{-Rt} \]

\[ R \sim e^{-\Delta G/kT} \]

Aggregation Probability

\[ P_A(\tau) = 1 - e^{-R\tau} \]
Aggregation:
- Fastest at End of Rectangle
- Slowest on Face of Square
- Even on Sides

Mesocrystal State 1:
- Most Frequent

Mesocrystal State 2:
- Occurs on Square

Mesocrystal State 3:
- Not Typically Frequent

Nanocrystal Encounters: Frequency of Outcomes

- Aggregation is the Most Frequent
- On the Smallest Facets, Perpetuating 1D Growth
Disruption Solvent Ordering at Edges Leads to Fast Aggregation on Small Facets
Conclusions

Solvent Ordering Around Nanocrystal Surfaces Promotes Growth of 1D Nanostructures

Leads to Mesocrystal States

Faster Aggregation on Smaller Facets
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Jin Pyo Hong
Dr. Ya Zhou
Dr. Yangzheng Lin

Alums
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Victor Gonzalo Ruiz Lopez
Matthias Scheffler

Univ. of Pittsburgh
Dr. Wissam Al-Saidi

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