Electronic Interactions and Double-Layer Charging for Supported Catalyst Nanoparticles Disentangled by Density-Potential Functional Theory

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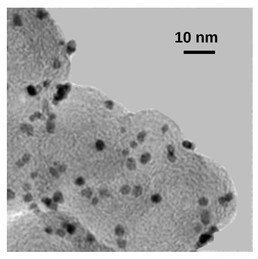
1. Background

- Supported nanoparticles (NPs) are widely used in technical devices reliant on catalysis.
- Support materials interact actively with metal NPs and greatly impact catalytical activity.
- Electron redistribution occurs between NP and support to achieve electronic equilibration. Its impact on NP's active surface in contact with electrolyte needs to be explored[2].
- Charging features of the electric double layer (EDL) of supported NP system is different from planar electrode and is awaiting investigation.



[1]

2. Methodology

- **Density-potential functional theory**[3]

Electron density: n_e Electric potential: ϕ

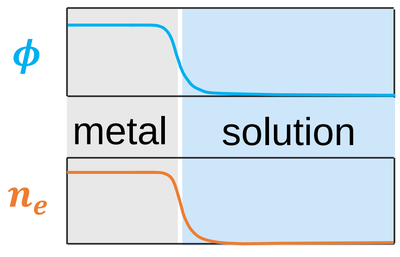
Free energy functional of the metal-solution interphase

$f = f_{\mathrm{qm}}[n_e, \nabla n_e]$ quantum mechanical part

$+ f_{\mathrm{c}}[\phi, \nabla\phi, \{n_i\}]$ classical part

$+ f_{\mathrm{inter}}[n_e, \phi, \{n_i\}]$ quantum-classical interactions

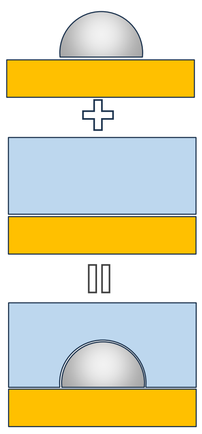
$- \sum_i n_i \mu_i$ grand-canonical



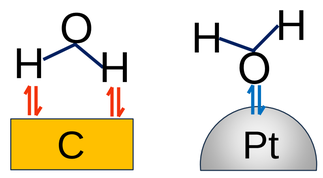
- Continuum, not atomistic model
- Metal ionic charges: uniform background
- Metal electrons: Thomas-Fermi
- Electron spillover at interface captured
- Solution: modified Poisson-Boltzmann

- **Workflow**

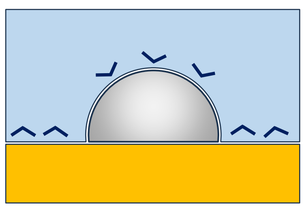
1. Extension (geometric complexity)



2. Calibration (chemical complexity)

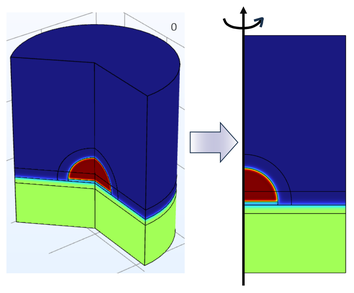


Metal-water interactions



3. Implementation

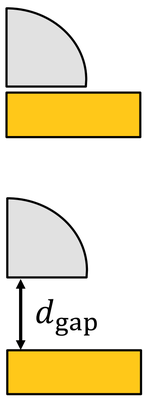
3D Cartesian 2D cylindrical

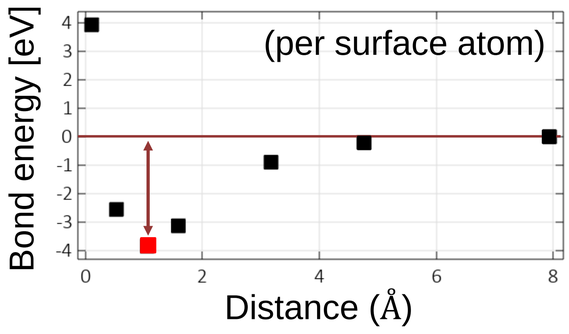


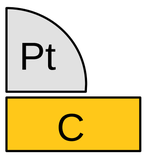
Axial symmetry

- **Structural relaxation**

Bond energy is dictated by the interplay of quantum-mechanical Pauli repulsion and electrostatic attraction

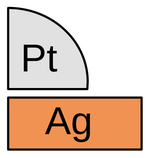






$d_{\mathrm{gap}} = 0.95$ Å

$E_{\mathrm{bond}} = 4.0$ eV (per surface atom)



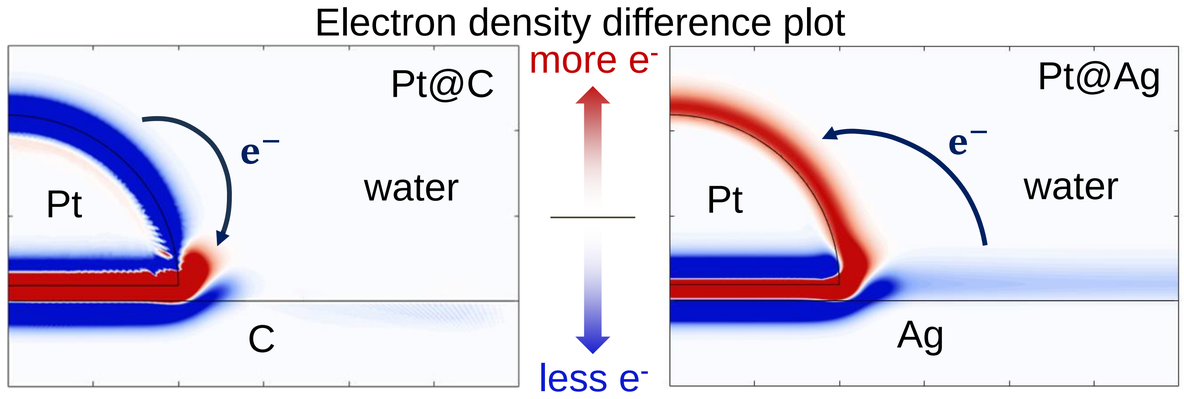
$d_{\mathrm{gap}} = 1.00$ Å

$E_{\mathrm{bond}} = 3.1$ eV

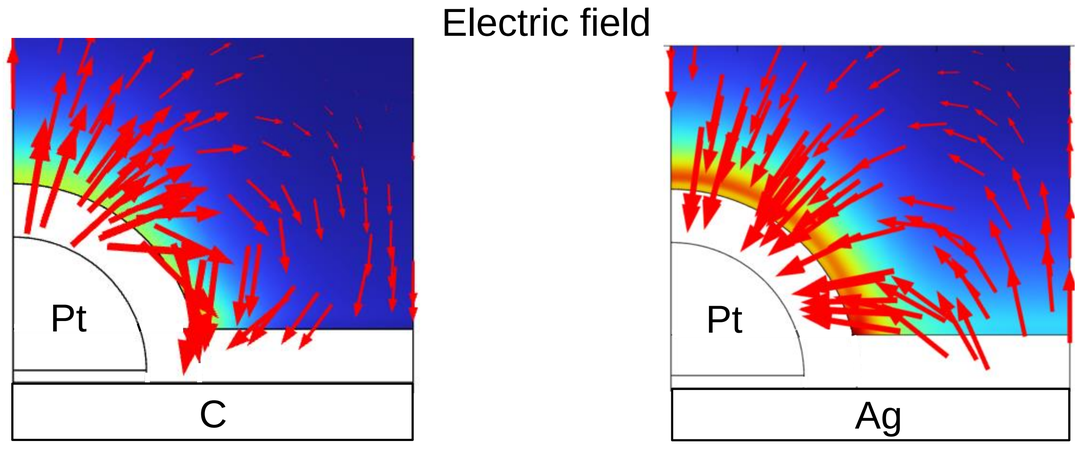
3. Results

- Electrification upon contact between NP and support due to electron redistribution

Electron density difference plot

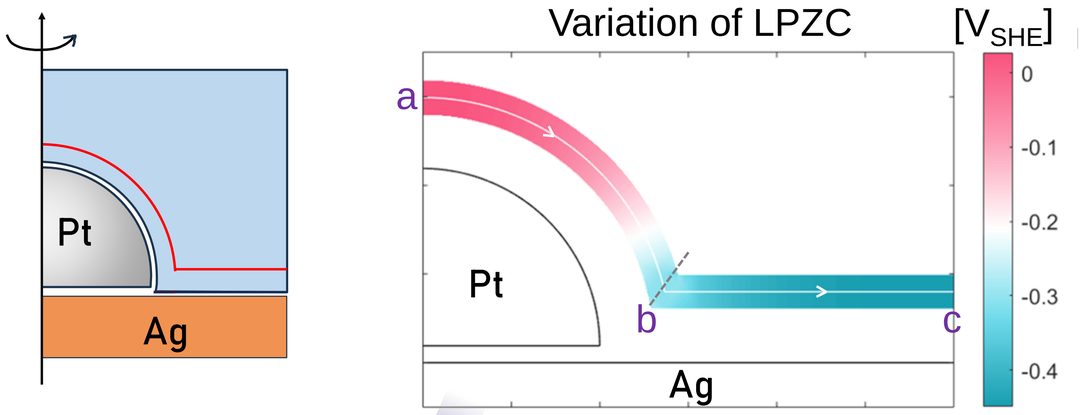


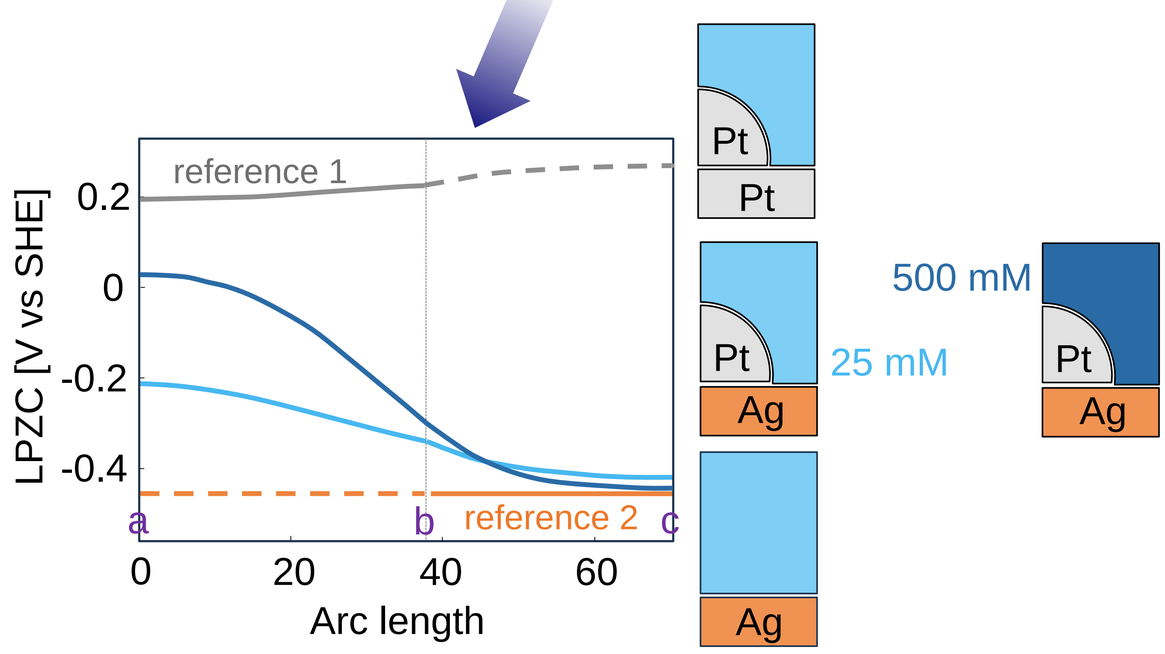
Electric field



For Pt@C and Pt@Ag, different electron redistributions lead to distinct electric field directions.

- Local potential of zero charge (LPZC) for supported NP system





LPZC affects local reaction environment which is significant for catalytic activity.

4. Take-home messages

- Electron redistribution in supported NP system induces an electric field, which gives a variation of local potential of zero charge.
- Local potential of zero charge, significant to local reaction conditions, can be regulated by using a suitable support material.

Acknowledgement

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References

[1] T. Binninger et al., J. Electrochem. Soc., 163, 10 (2016)
[2] T. Binninger et al., Phys. Rev. B, 96, 165405 (2017)
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