

Turning CO₂ into Biofuels using Copper Nanoparticles

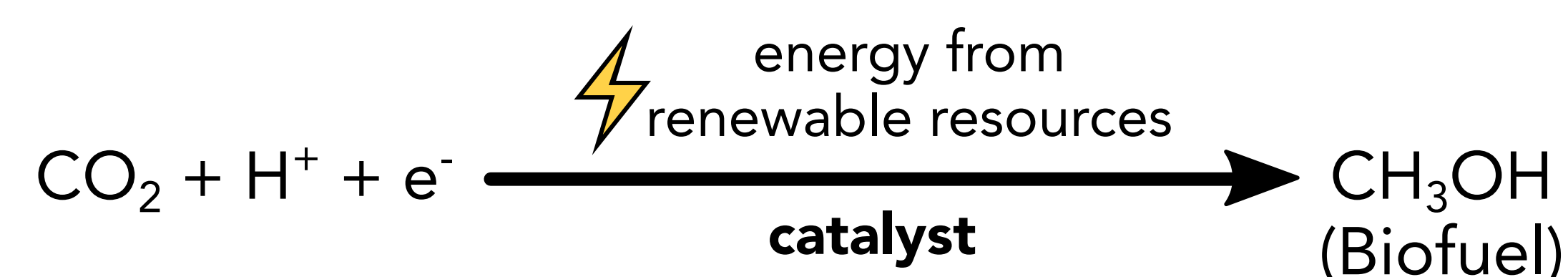
Geoffrey R. Weal,^{a,b} Kristinn I. Guðmundsson,^c Frank D. MacKenzie,^{a,b} John R. Whiting,^{a,b} Nicholas B. Smith,^{a,b} Egill Skúlason,^c and Anna L. Garden^{a,b}

^a Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand; ^b The MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, P.O. Box 600, Wellington 6140, New Zealand; ^c Science Institute and Faculty of Industrial Engineering, Mechanical Engineering and Computer Science, University of Iceland, VR-III, 107 Reykjavík, Iceland.

Motivation

Carbon dioxide (CO₂) emitted from fossil fuels is changing our climate. Fossil fuels are primarily used in transportation because they are portable fuels. **Producing portable fuels from renewable energy resources** is vital for curbing our reliance on fossil fuels.

Biofuels are portable fuels made from CO₂ and renewable resources



Biofuels require a catalyst to be produced at rates required for production

Copper (Cu) nanoparticles may be the solution^{1,2}

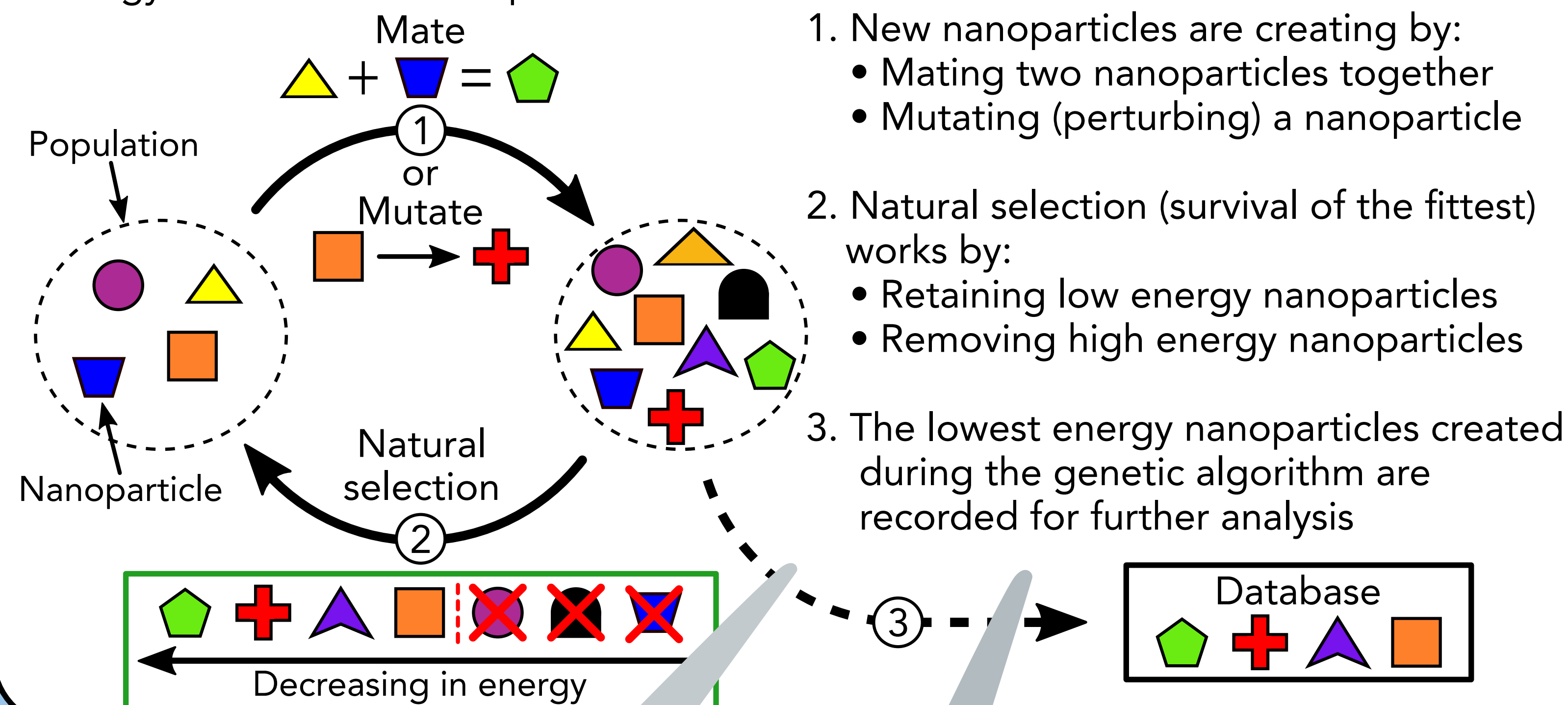
Aim

To understand the catalytic properties of Cu nanoparticles between 55 and 147 atoms in size **using computational chemistry techniques.**

Biofuels are carbon-neutral fuels because they are made with CO₂ from the atmosphere. **Biofuels do not release new CO₂ into the atmosphere.**

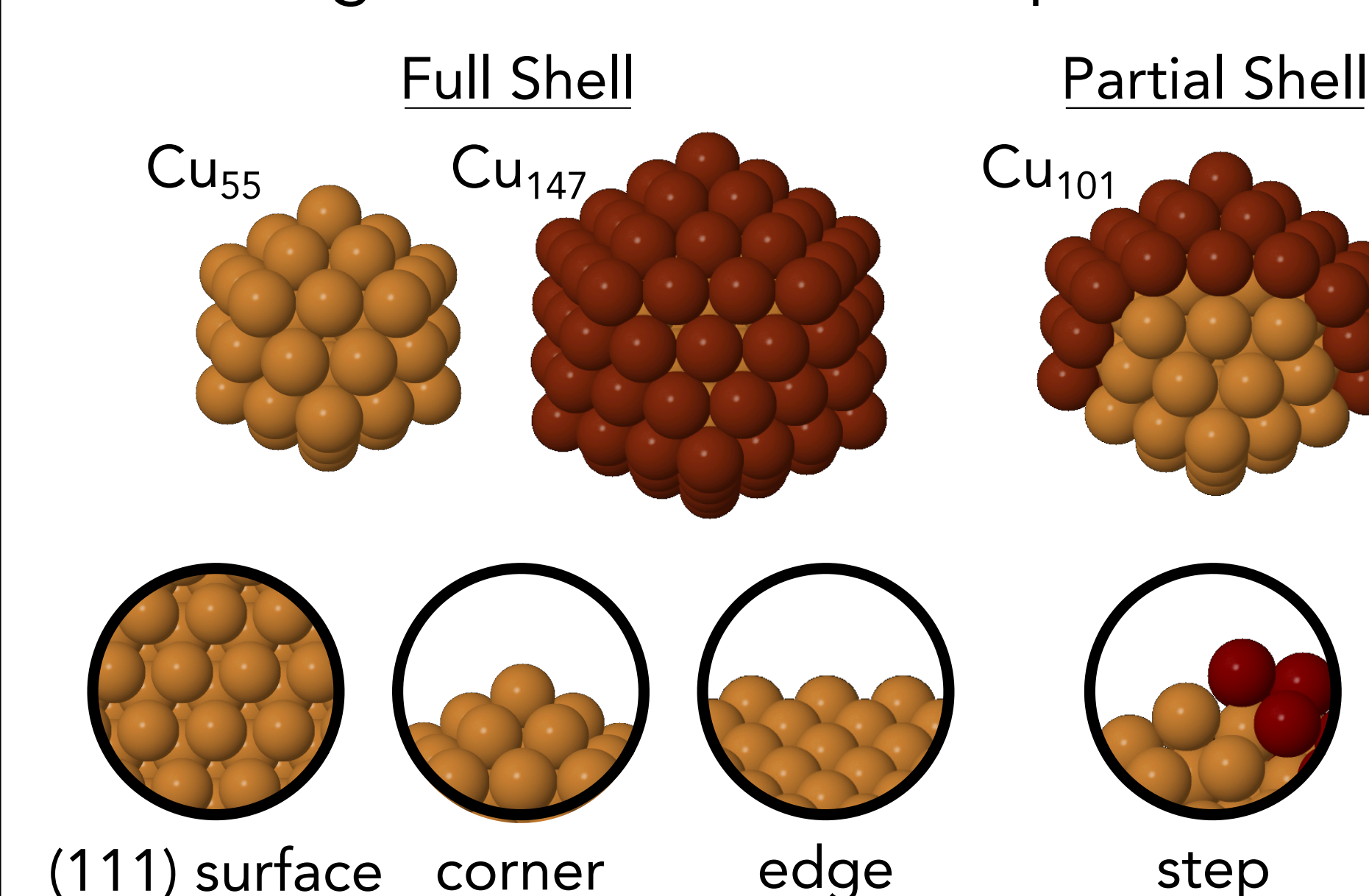
Obtaining Representative Low Energy Cu Nanoparticles

The genetic algorithm uses Darwin's Theory of evolution to obtain representative low energy models of Cu nanoparticles.³

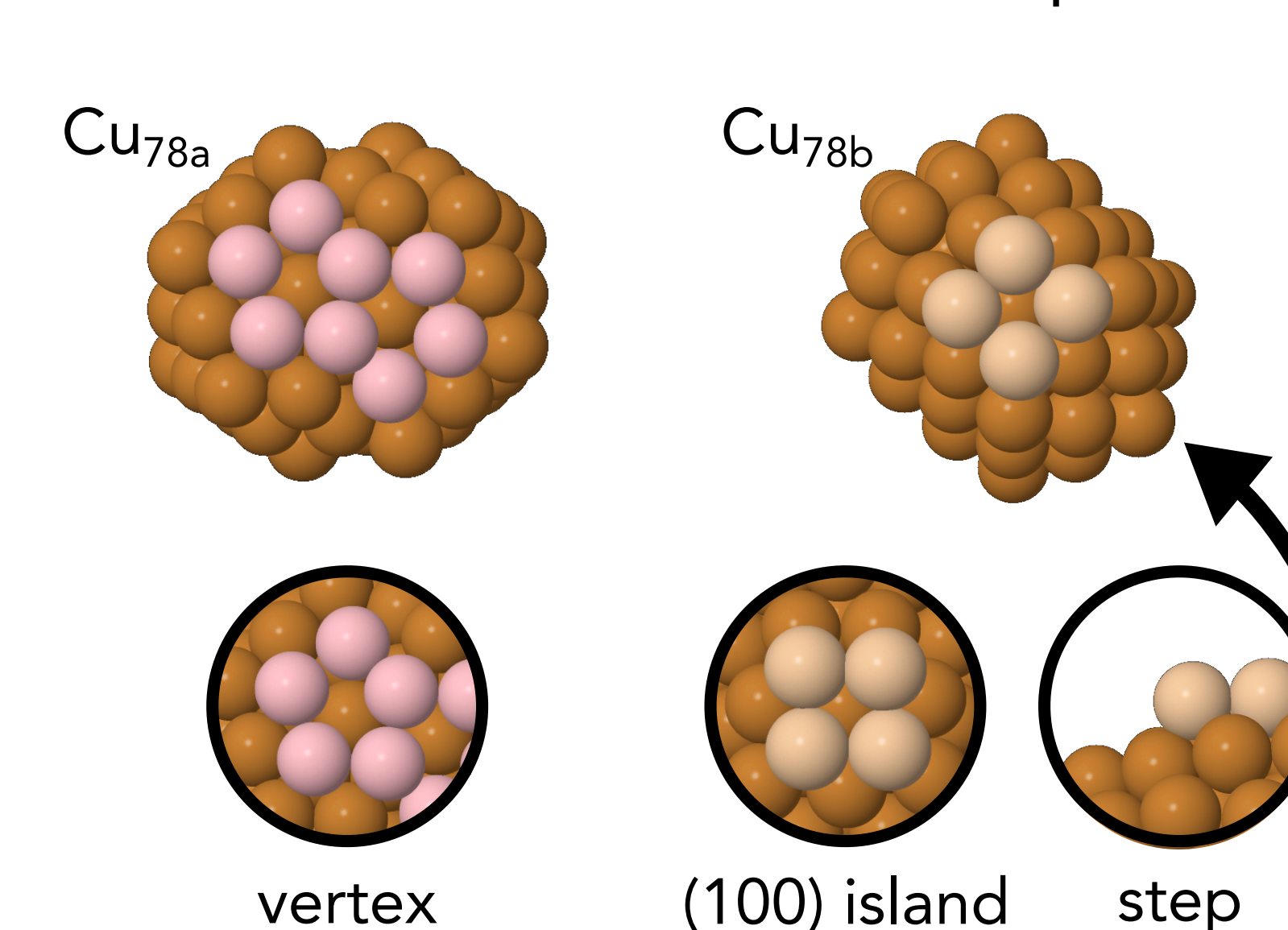


The lowest energy Cu nanoparticles were regular or distorted icosahedral nanoparticles that contained interesting surface features. **These surface features may be catalytically advantageous.**

Regular icosahedral nanoparticles



Distorted icosahedral nanoparticles

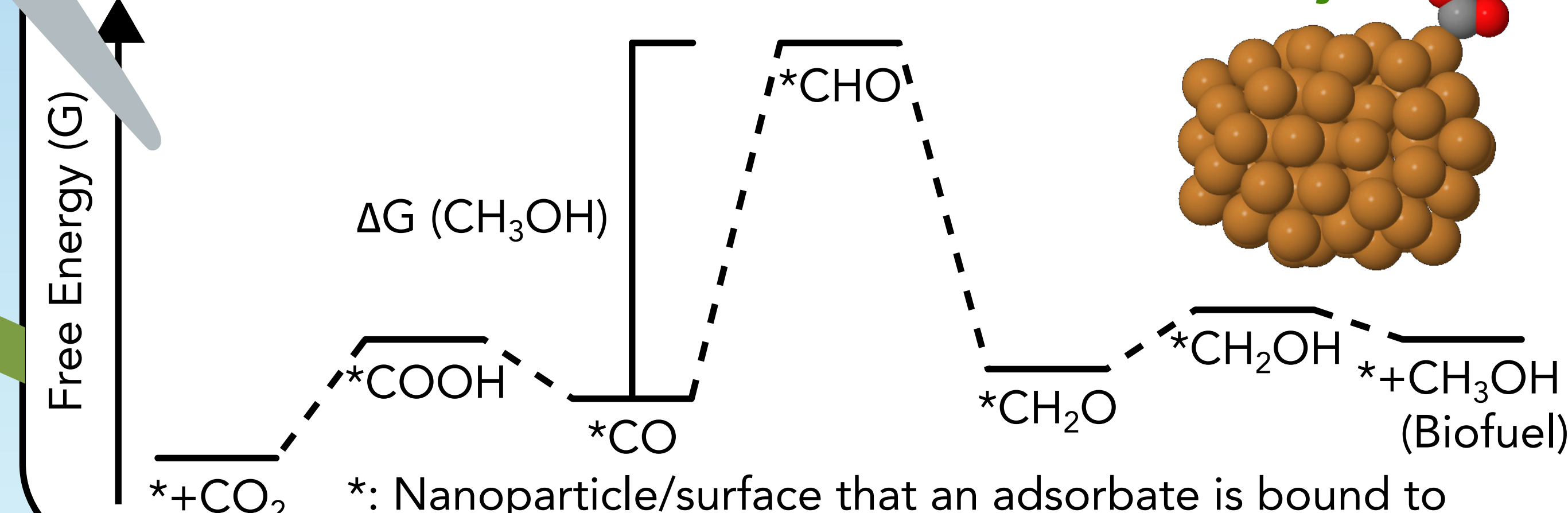


Studying the Catalysis of CO₂ to CH₃OH with Cu Nanoparticles

The mechanism from CO₂ to CH₃OH is multi-stepped. We studied the **preferential binding sites of intermediates upon Cu nanoparticles, as well as other Cu surface models.**

Free energy diagrams indicated the **thermodynamically limiting step, ΔG**, which is the **greatest uphill step** in the mechanism. For every nanoparticle and surface studied, this was the *CO → *CHO step.

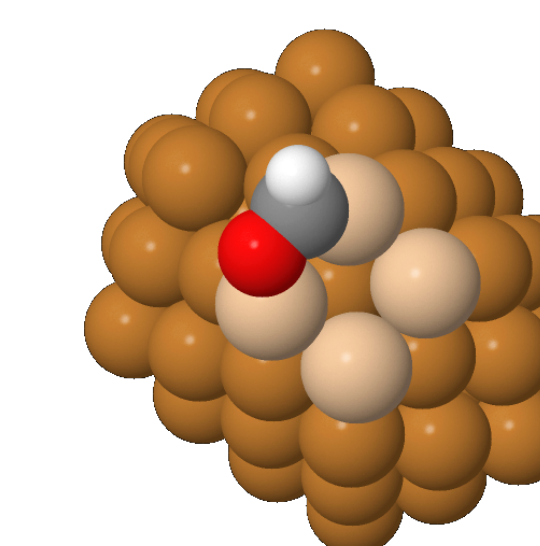
A smaller ΔG can indicate a faster and better catalyst



Nanoparticle/surface	ΔG (CH ₃ OH) / eV
Surface models (control)	0.66 - 0.76
Most Cu nanoparticles	0.66 - 0.81
Cu_{78b}	0.39

Cu_{78b} had the smallest ΔG value

Why?



The (100) island allows CHO to comfortably bind across adjacent Cu atoms. This minimises the binding energy of CHO, which lowers ΔG for Cu_{78b}.

1. D. Kim, C. S. Kley, Y. Li, P. Yang, *Proc. Natl. Acad. Sci. U.S.A.* 2017, 114, 40, 10560 - 10565
2. H. Dong, C. Liu, Y. Li, D. Jiang, *Nanoscale* 2019, 11, 11351 - 11359
3. G. R. Weal, S. M. McIntyre, A. L. Garden, *J. Chem. Inf. Model.* 2021, 61, 4, 1732 - 1744

otago.ac.nz/annagarden
@GardenGroupUO
github.com/geoffreyweal
See github.com/Adsorber:
A program for binding adsorbates to models.