Copper Nanopyramids Promote C-C Coupling and Enable Electroreduction CO_2 to Valuable C_{2+} Chemicals

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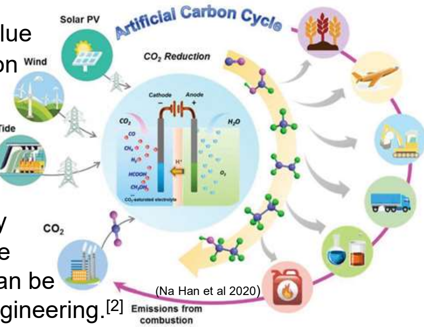
Background

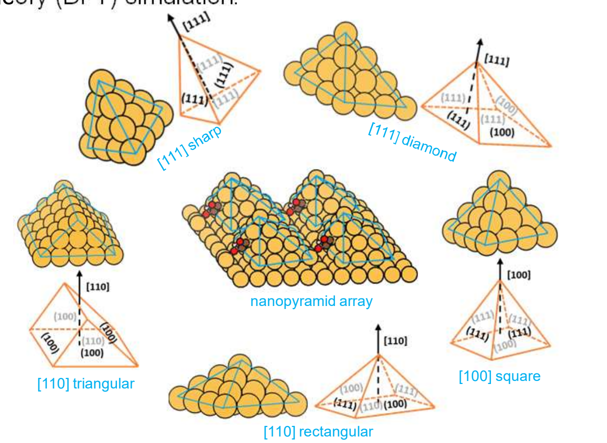
- **C**onverting CO_2 to high-value hydrocarbon by CO_2 Reduction Reaction attracted attentions due to higher energy density, readiness for transportation & utilization infrastructure.[1]
- **P**oor selectivity & efficiency make Cu incapable of effective reduction CO_2 to C_{2+}, which can be improved by nanostructure engineering.[2]



- **T**ailoring the copper catalyst morphology by forming nanopyramids offers method to promote C-C coupling and enables the direct production of valuable C_{2+} chemicals.[3-4]

Modelling

- **M**olecular modelling powered by Density Functional Theory (DFT) simulation.



Results

- **E**xclusive to nanopyramid catalysts, pyramidal effect has three aspects, which are improved *CO adsorptions, geometrically preferable sites for C-C coupling and enhanced electron transfer from surface.
- **A**nomalous C-C coupling activity induced by pyramidal effect leads to new C_2 active sites, and significantly promotes C_2 selectivity on under-coordinated Cu (111) surface.
- **T**his new active site can be predicted by an effective C_2 active site screening principle-the extended 'square' principle, which further serve as morphology design rule for efficient catalyst (Figure 1,2).

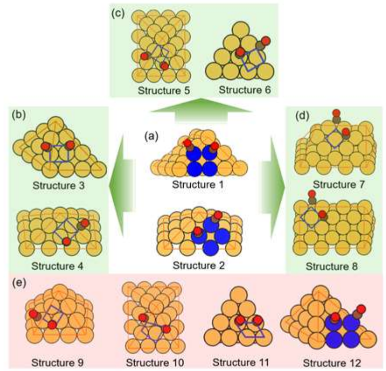


Figure 1. Application of extended 'square' principle.

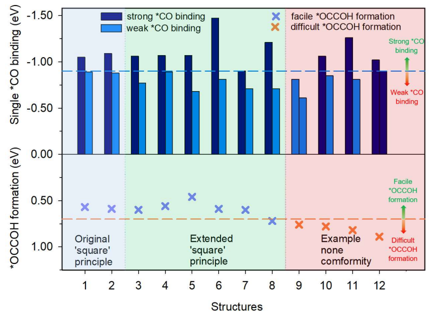


Figure 2. $E^{*CO}_{Adsorption}$ and $E^{*OCCOH}_{Formation}$ of structures

- **N**anopyramids significantly favor C_2 production.

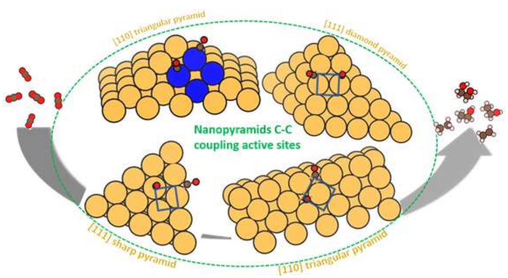


Figure 3. Cu nanopyramids drive selectivity over C_2 formation.

Results (continued)

- **D**ensely arrayed nanopyramids incur confined space and the resultant O-Cu bond with adjacent nanopyramids.
- **S**uch atomic arrangement further facilitates C-C coupling (Figure 3).

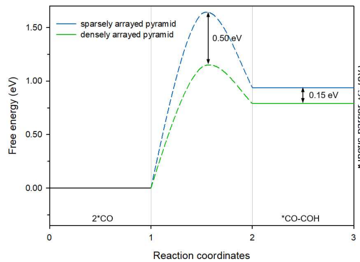


Figure 3. C-C coupling energetics on densely and sparsely arrayed nanopyramids

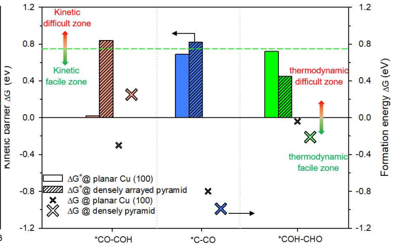


Figure 4. Formation energetics of intermediates on Cu (100) and densely arrayed nanopyramids

- **T**he space confinement effect disadvantages competing pathways (Figure 4), and keep C-O bonds intact against dihydroxylation thus enable a low-energetics pathway to direct electrosynthesis of ethylene glycol (Figure 5).

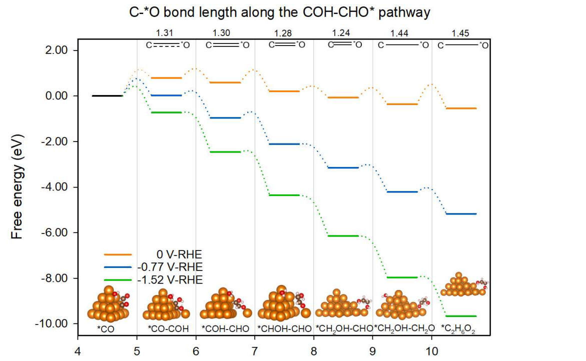


Figure 5. Reduction of *CO to ethylene glycol on densely arrayed nanopyramid.

Conclusions

- **C**u nanopyramid exhibits significant C_2 selectivity and it is also a promising catalyst for direct production of some C_{2+} chemicals.

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References

1. Y. Jiao, Y. Zheng, M. Jaroniec, S. Qiao, *Chem. Soc. Rev.*, **2015**, 44, 2060-2086.
2. Y. Zheng, A. Vasileff et al, *J. Am. Chem. Soc*, **2019**, 141, 7646-7659.
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