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CO_2 electroreduction toward C_2H_4 at Cu decorated graphene nanofilm: Prediction from first principles

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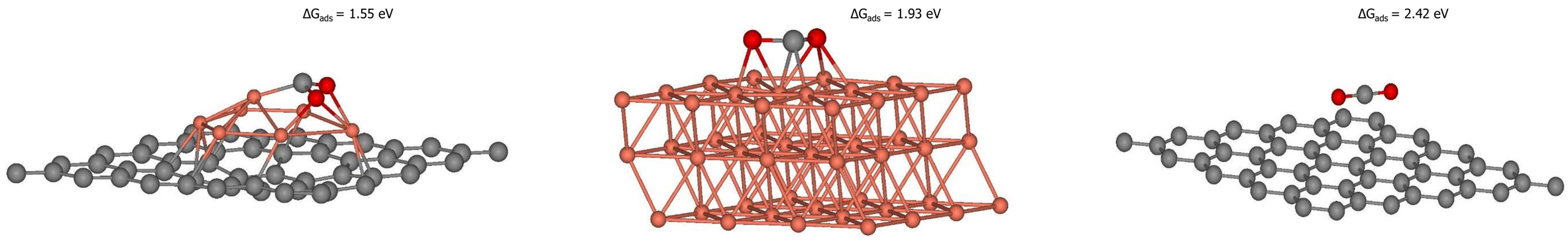
Introduction

The electrochemical reduction of CO_2 is a promising green approach to convert CO_2 into usable form of carbons. Unlike the conventional thermal catalysis method where high pressure and high temperature are needed to initiate the reaction, the electrochemical reduction reaction can proceed in ambient environments and the reaction can in principle achieve much higher selectivity. In this respect monodisperse Cu nanoparticles assembled on a single layered graphene can support mass- and size-dependent catalysis for the selective electrochemical reduction of CO_2 to ethylene (C_2H_4). The properly treated (e.g. N-doped) graphene itself can catalyse the CO_2 reduction to formate, but the composite graphene-Cu structure functions as a CO_2 and proton absorber, facilitating hydrogenation and carbon–carbon coupling reactions on Cu-nanocluster for the formation of C_2H_4.

In the present study, we employ density functional theory calculations to examine different active sites in Cu-decorated graphene, to give an outline of the trends in its catalytic activity. We found that adsorption energies of CO_2 and CH_2 do not follow the linear scaling relationships observed for the pure transition metals, and this unique scaling is rationalized through differences in electronic structure between transition metals and graphene. This finding rationalizes most of the experimental observations on the carbon-based materials which present promising catalysts for the two-electron reduction of CO_2 to CO. With thermodynamic analysis, we identify active sites that are expected to exhibit a comparable or even better activity to the state-of-the-art copper catalysts, and the best configurations are suggested to be selective for CO_2 reduction reaction.

Results:

CO_2 adsorption on Cu_7@graphene nanostruture:

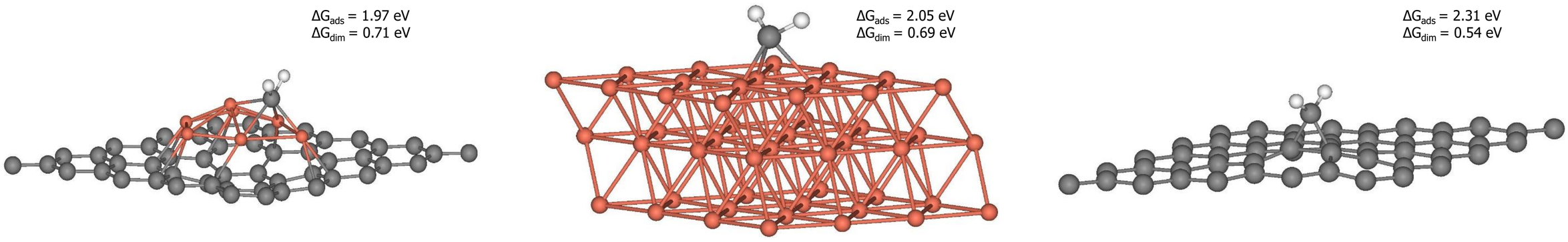


- CO_2 can be electrochemically reduced to hydrocarbons such as ethylene and methane via $2CO_2 + 12e^- + 8H_2O \rightarrow C_2H_4 + 12OH^-$ and

  $CO_2 + 8e^- + 6H_2O \rightarrow CH_4 + 8OH^-$
- CO_2 adsorption is the rate-determining step in CO_2 reduction reaction, and thus it is desirable to find/design catalyst sites that bonds CO_2 stronger than H adsorption (ΔG_{ads} = 2.93 eV)
- The stronger binding of CO_2 to the Cu_7 nanocluster we explain by the presence of wide <111> grain boundaries region on the Cu_7 nanocluster with respect to Cu (111) surface. Experimentally measured enhancement in Faraday efficiency of generating multi-carbon hydrocarbons is correlated with the density of the Cu catalyst grain boundary areas*. The adsorption properties of neighboring Cu sites are significantly perturbed by the presence of nearest C, and the stronger Cu-O bonding is formed on the catalyst surface, which also can enhance $H_2C{=}CH_2$ evolution.

* X. Feng, K. Jiang, S. Fan and M. W. Kanan, ACS Cent. Sci., 2016, 2, 169–174.

CH_2 dimerization on Cu_7@graphene nanostruture:



- The most probable pathways for C_2H_4 formation is that one that shares an intermediate with the pathway to CH_4.
- The $*CH_2$ dimerization is a crucial step for the final C_2H_4 production ("carbene" mechanism).
- The lowest dimerization barrier is predicted for the pristine graphene due do lowest free adsorption energy

Conclusions

Cu cluster at graphene reproduce the facets of the most stable Cu(111) surface. In agreement with recent experimental observations, we predict the stronger binding of CO_2 to the Cu_7 nanocluster due the presence of wide <111> grain boundaries region on the Cu_7 nanocluster with respect to Cu (111) surface. Based on this we predict the larger is the length of grain boundaries of the Cu_n nanocluster deposited at graphene the more selective to the C_2H_4 could be the catalyst

The lowest dimerization barrier is predicted for the pristine graphene due do lowest free adsorption energy, meaning that the whole CO_2 reduction reaction taking place at the grain boundary of Cu_n@graphene nanocluster may lead to improved selectivity to ethylene.

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