# Theoretical Perspective on Electronic Factors Promoting C-C Coupling for $CO_2$ Reduction Reaction on Graphyne Surface

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Electrochemical $CO_2$ reduction reaction (CRR) offers a promising route to produce fuels and value-added chemicals within a sustainable energy cycle. Due to their higher energy density, the efficient synthesis of multi-carbon products, such as ethylene, ethanol, or propanol, has attracted great interest. On the copper surface, the carbon-carbon (C-C) coupling reaction between two CO molecules (2*CO→*OC-CO) has been reported to be the bottleneck. Therefore, we need CO binding at neighboring catalyst sites with low C-C coupling barriers.

In the present talk, we tackle this problem from two perspectives: 1) how to promote two CO binding on neighboring reaction sites, and 2) how to utilize an oriented electric field for efficient C-C coupling reaction. We focused on transition metal doping of graphyne, a novel material that replaces selected bonds in 2D graphene with acetylenic groups, resulting in a mixed sp-$sp^2$ hybrid carbon allotrope. Utilizing density functional theory calculations, we show that pi- (C≡C) and d- (Co) orbital active centers with a spillover mechanism can actively produce two neighboring *COs from two $CO_2$ molecules. Furthermore, the estimated activation barrier of 0.47 eV shows high reactivity at room temperature. In addition, the application of an electric field perpendicular to the 2D-graphyne surface was shown to decrease the C-C coupling barrier by ~0.5 eV per 1 V/Å. Considering that electric fields at the electrodes in CRR are in the range of 0.5 to 1 V/Å, these electric fields can actively promote C-C coupling reaction on graphyne based catalysts.

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