CO_2 REDUCTION

Dimers on the way

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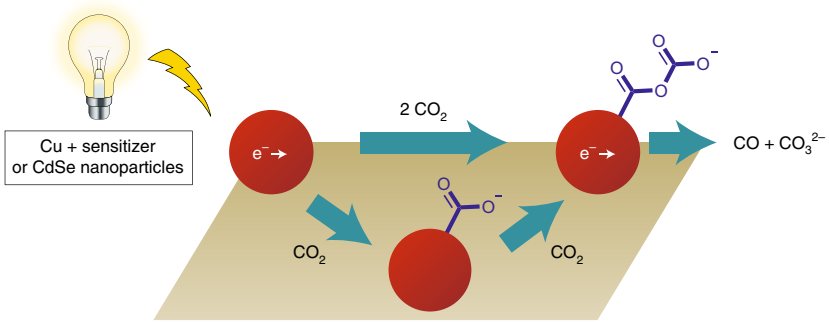

Catalytic CO_2 reduction is an important technology for the production of fuels and chemicals. Mechanistic studies have suggested that both electro- and photocatalytic approaches may share a common intermediate, namely a carbon dioxide radical anion (CO_2^-) bound to the catalyst's surface.

Now, using rapid-scan Fourier-transformed infrared spectroscopy in combination with isotopic labelling, Heinz Frei and co-workers identified a carbon dioxide dimer radical anion ($C_2O_4^-$) as the crucial surface intermediate during the photocatalytic reduction of CO_2 on copper nanoparticles. Although recent electrochemical investigations have suggested the existence of this one-electron surface intermediate, this study provides its first direct experimental evidence.

In a second set of experiments the authors were also able to show a correlation between the decay of the spectral signals associated with the CO_2 dimer species and the growth of the CO and CO_3^{2-} signals; those two being disproportionation products of the surface-bound intermediate. In this case, however, they employed a different catalyst, as the copper-nanoparticle-based system does not allow the monitoring of CO and $C_2O_4^-$ on the same timescale due to the limited spectral sensitivity. In fact, the group performed the reaction using cadmium selenide nanoparticles (pictured), providing complementary evidence for the existence of $C_2O_4^-$ on different catalytic materials. As the growth of the carbon dioxide dimer radical anion does not show an induction period on the timescale of seconds, the authors suggest that any CO_2^- species possibly formed could further evolve into $C_2O_4^-$ on a very fast timescale by reaction with a second CO_2 molecule. On the other side, compared to the traditional path for CO_2 reduction, which only implies a surface-bound carbon dioxide radical anion, a direct dimer route is estimated to be energetically more favourable.

This study could have important implications for the design of catalysts with superior performance, as in principle CO_2 reduction efficiency can be improved by enhancing the formation of surface-bound dimers. To this end, one approach could be the combination of the nanoparticles with supports that feature high CO_2 adsorption capacity.

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