

Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel

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Background:

What is electroreduction of CO₂?

This is the conversion of CO₂ to more reduced chemical species using electrical energy.

What are the advantages?

We can get organic feedstocks and also global carbon balance.

What are the disadvantages?

This process requires high overpotential.

Different types of electrocatalysts

Metal, metal alloys, metal oxides, metal complexes, polymers/clusters, enzymes and organic molecules.

So now a days the catalyts' activity, product selectivity, Faradaic efficiency, catalytic stability and reduction mechanisms during CO₂ electroreduction have received detailed treatment. There are also the effects of electrode potential, solution-electrolyte type and composition, temperature, pressure, and other conditions on these catalyst properties.

INTRODUCTION:

- ❖ Representing a potentially clean strategy the electroreduction of CO_2 into useful fuels replaces fossil feedstocks and deals with increasing CO_2 emissions and their adverse effects on climate.
- ❖ The critical bottleneck lies in activating CO_2 into the $\text{CO}_2^{\cdot-}$ radical anion or other intermediates that can be converted further, as the activation usually requires impractically high overpotentials.
- ❖ Recently, electrocatalysts based on oxide-derived metal nanostructures have been shown to enable CO_2 reduction at low overpotentials. However, it remains unclear how the electrocatalytic activity of these metals is influenced by their native oxides.

In this paper.....

- To evaluate the role of the two different catalytic sites, they have fabricated two kinds of four-atom-thick layers: pure cobalt metal, and co-existing domains of cobalt metal and cobalt oxide.
- They found that surface cobalt atoms of the atomically thin layers have higher intrinsic activity and selectivity towards formate production, at lower overpotentials, than do surface cobalt atoms on bulk samples.
- Thus partial oxidation of the atomic layers further increase their intrinsic activity, which outperforms previously reported metal or metal oxide electrodes evaluated under comparable conditions.

SYNTHESIS AND CHARACTERIZATIONS:

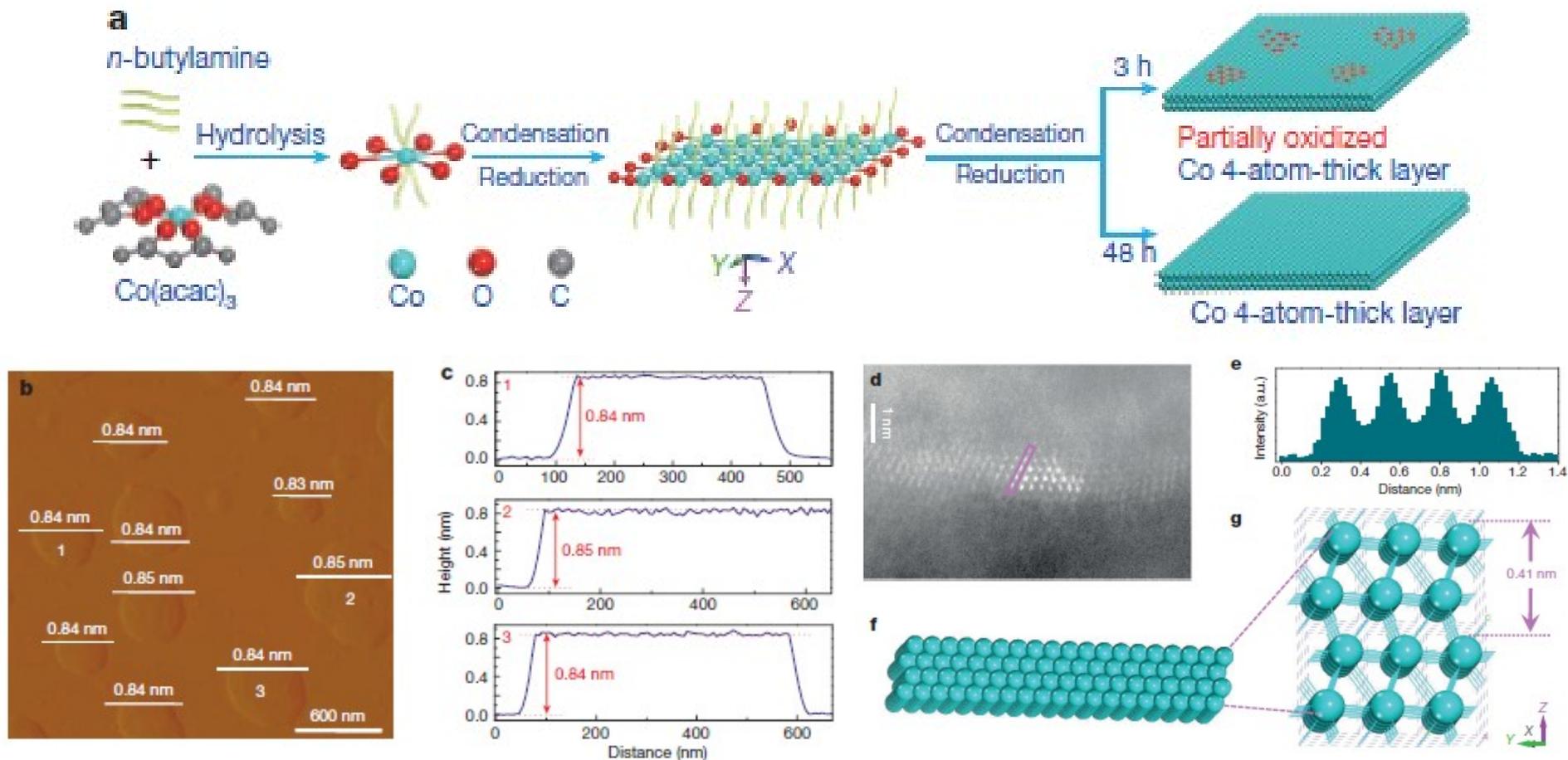


Figure 1: a, Schematic formation process of the partially oxidized and pure-Co 4-atomic-layer, respectively. b-g, Characterizations for the partially oxidized Co 4-atomic-layers: atomic force microscopy image (b) height profiles (c) lateral HAADF-STEM image (d) corresponding intensity profile along the pink rectangle in d, directly showing the 4-atom thickness of the layer (e) crystal structures (f, g).

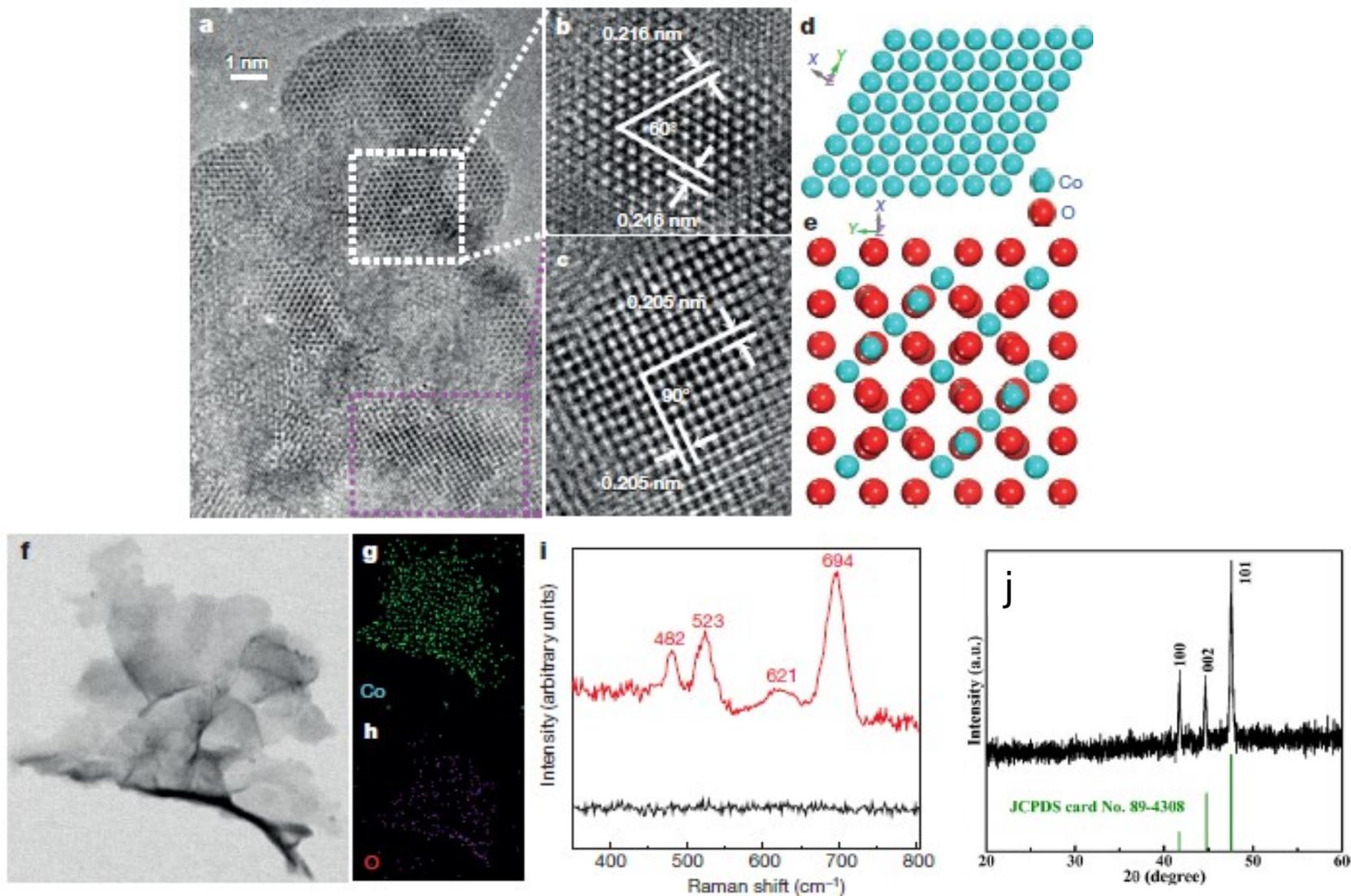


Figure 2: a, High-resolution TEM image. b, c, Enlarged high resolution TEM images. d, e, The related schematic atomic models, clearly showing distinct atomic configuration corresponding to hexagonal Co and cubic Co₃O₄. f-h, Elemental mapping. i, Micro-Raman spectra for the products obtained at 220 °C for 3 h (red line) and 48 h (black line). j, XRD pattern.

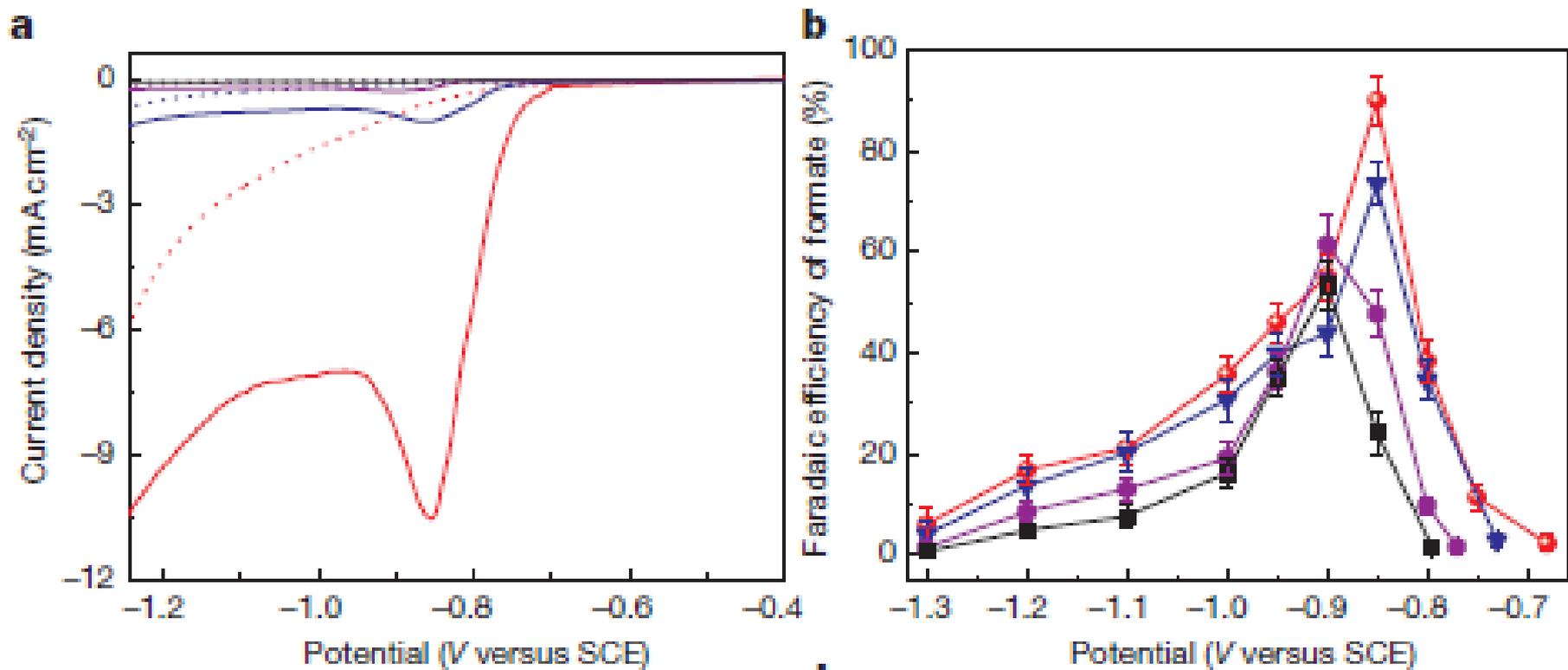


Figure 3: Electroreduction of CO₂ to formate for partially oxidized Co 4-atom-thick layers (red), Co 4-atom-thick layers (blue), partially oxidized bulk Co (violet) and bulk Co (black). a, Linear voltammetric curves in a CO₂-saturated (solid line) and N₂-saturated (dashed line) 0.1 M Na₂SO₄ aqueous solution. b, Faradaic efficiencies of formate at each given potential for 4 h.

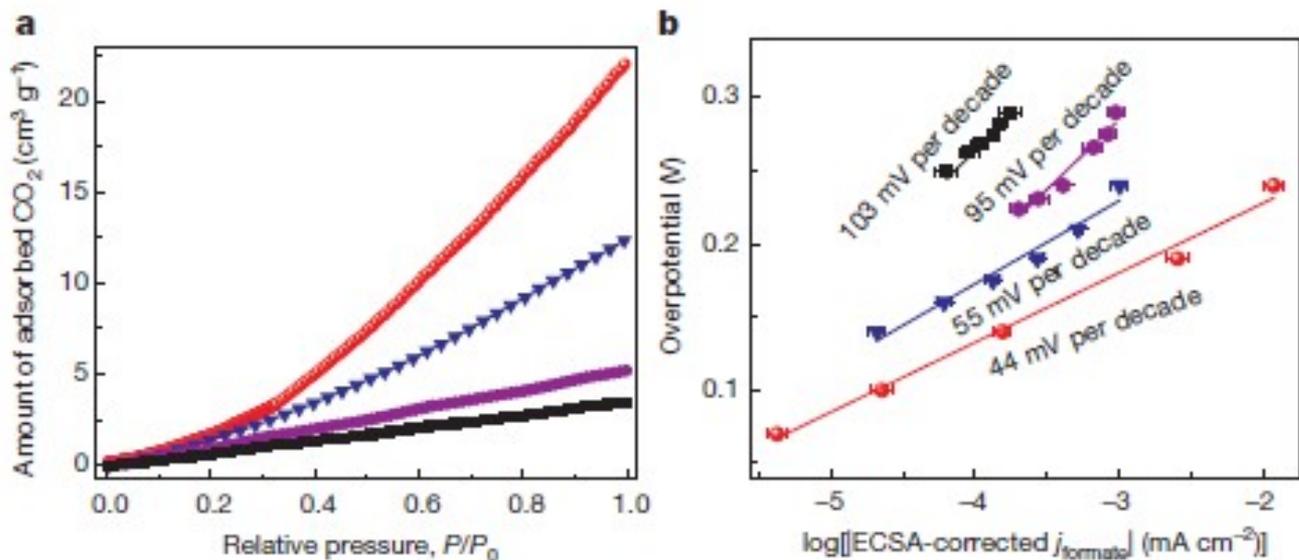


Figure 4: a, CO₂ adsorption isotherms. b, ECSA-corrected Tafel plots for formate production. j_{formate} is the partial current density of producing formate.

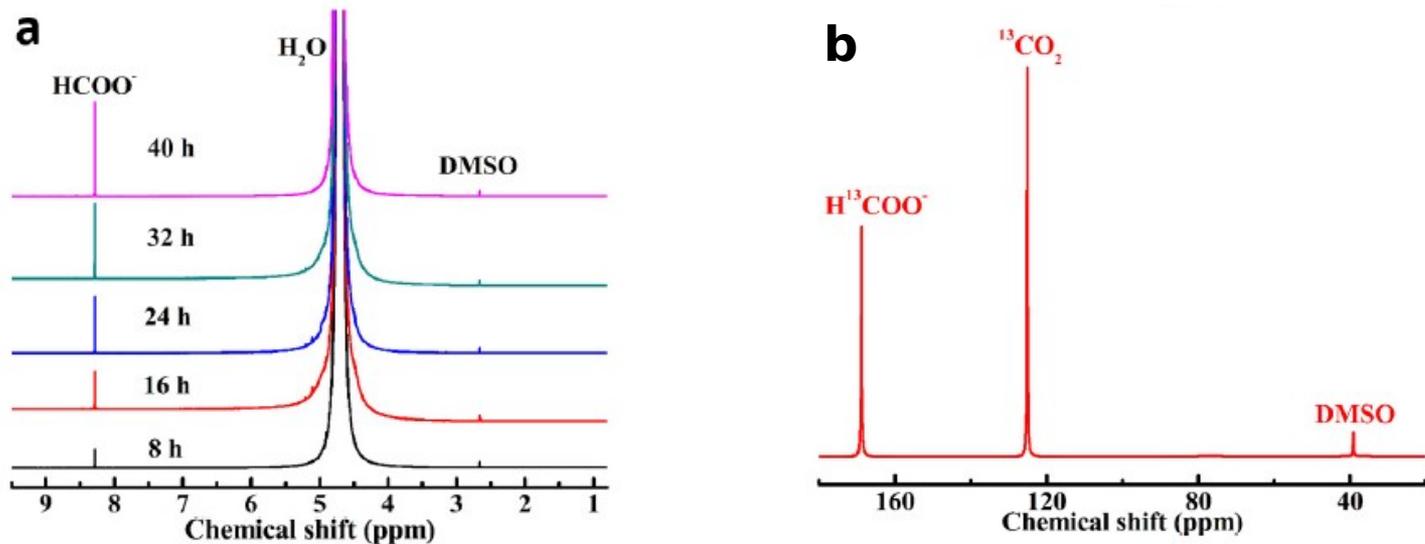


Figure 5: NMR spectra a, ¹H-NMR and b, ¹³C-NMR of formate yield for the partially oxidized Co 4-atom thick layers. DMSO is used as an internal standard for quantification of HCOO⁻.

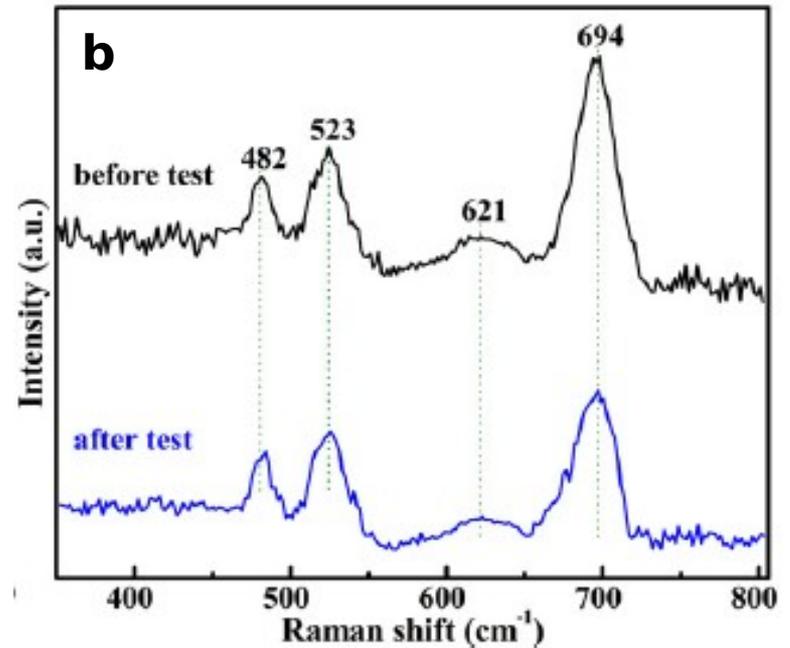
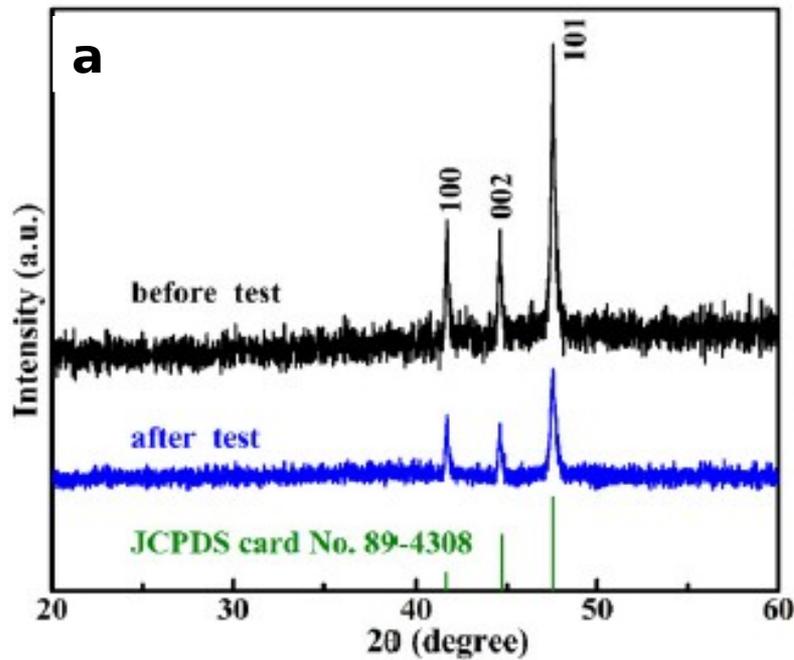


Figure 6: a, XRD patterns b, Raman spectra for the partially oxidized Co 4-atom-thick layers before and after the 40-h CO₂ reduction test.

CONCLUSIONS:

- This synthetic strategy has allowed to produce a well controlled model system to explore the influence of both atomic-scale structure and the presence of an oxide on the activity of a metal catalyst.
- It also clearly demonstrate that Co-based catalysts in the form of 4-atom-thick layers exhibit higher intrinsic activity for formate production at lower overpotentials than the bulk material, and that partial oxidation improves the intrinsic activity of the system significantly further.
- Thus the appropriate morphology and oxidation state can transform a material considered nearly non-catalytic for CO₂ reduction into a very active and robust catalyst.

FUTURE DIRECTIONS.....

Co_3O_4 is a semiconducting material and it also acts as a photocatalyst itself. But in this paper they did not mention anything about its photocatalytic property. So we can check its photocatalytic property or for some other metal oxides which can be synthesized by this way.

THANK
YOU...