Hybrid atomic layers based electrocatalyst converts waste CO₂ into liquid fuel

Yadong Li

Electrocatalyst that converts carbon dioxide to useful fuels, using electricity generated from renewable sources, is generally regarded as a potentially “clean” strategy of turning trash into treasure under mild conditions [1,2]. Lots of studies have demonstrated that electroreduction of CO₂ contains several elementary steps of adsorption, activation, dissociation and desorption, among which the most critical bottleneck lies in the activation of CO₂ to form CO₂^{•−} or other intermediates [3–6], which usually requires very high overpotentials. In this case, worldwide scientists have made great efforts to lower the activation energy barrier of CO₂.

Some scientists recently found that electrocatalysts based on oxide-derived metal nanostructures showed much lowered CO₂ reduction potentials compared with the pristine metal nanostructures [3,7,8]. For instance, it was found that the Cu₂O-derived Cu film electrode exhibited a 0.5 V less overpotential and over 10 times larger current density as well as higher product selectivity in comparison with the polycrystalline Cu electrode [8]. However, it should be noted that atomic-level insight into the correlation between the pre-existing metal oxide and CO₂ reduction of its native metal is still an open question. The possible reason may be that the presence of abundant microstructures such as surface, interface, and defect would adversely affect or cover the effect of metal oxide on CO₂ reduction activity of its native metal [9].

To unravel the question of how oxide matters in its native metal catalysis, Xie's and Sun's group from Hefei National Laboratory for Physical Sciences at Microscale, University of Science & Technology of China initially constructed an ideal model of intact metal atomic layer and hence deliberately created its oxide on the surface, forming an oxide/metal atomic layer catalyst model [10]. Benefiting from the atomic thickness, the built material model enabled most of the metal atoms or metal ions to distribute on the surface. In other words, the abundant surface metal atoms and metal ions could serve as the two typical active sites for involv-

ing surface catalytic reactions, hence providing the prerequisite for disclosing the crucial role of surface metal oxide in CO₂ reduction of its native metal.

In the paper published in *Nature* [10], Xie's and Sun's group fabricated freestanding 4-atom-thick Co sheets with surface Co oxide by virtue of a ligand-confined growth strategy (Fig. 1). Of note, both the dimethylformamide and *n*-butylamine were demonstrated to play an important role in reducing the metal ions and forming a two-dimensional (2D) sheet-like morphology. With the help of high-resolution transmission electron microscopy (TEM) images, Xie's and Sun's group disclosed that the majority of the 2D sheet corresponded to the [001]-oriented hexagonal Co. In addition, they also demonstrated that there was another domain of Co oxide that embedded in the Co metal 2D sheet (Fig. 2). Their statement was further confirmed by the corresponding elemental mapping and micro-Raman spectrum results. Atomic force microscopy determines that their fabricated hybrid 2D sheet possesses a thickness of ca. 0.84 nm, which is consistent with the 0.82-nm thickness of a 4-atom-thick Co slab along the [001] direction. More interestingly, they provided a direct evidence to demonstrate the 4-atom layer thickness of the synthetic hybrid two-dimensional sheet, as illustrated by the lateral high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image in Figs 1d and e.

According to electrochemical surface area-corrected Tafel plots and Faradaic efficiencies, Xie's and Sun's group stated that the atomic layers confined surface Co atoms showed the ability to largely change the intrinsic activity and selectivity toward formate production at low overpotentials compared with bulk counterpart, while their confined surface Co oxide favored further increased intrinsic activity for CO₂ reduction. As the anonymous reviewer has said, “This work takes a material which has been considered nearly non-catalytic for this reaction and demonstrates if placed in the correct morphology and oxidation

Department of Chemistry and Collaborative Innovation Center for Nanomaterial Science and Engineering, Tsinghua University, Beijing 100084, China
Email: ydli@mail.tsinghua.edu.cn

Figure 1 Schematic illustration for the electroreduction of CO₂ into formate over the partially oxidized Co 4-atomic-layers, and the corresponding potential applications in direct formic acid fuel cell, leatherworking, electroplating and airport snow-melting agent.

Figure 2 (a) High-resolution TEM image of the partially oxidized Co 4-atom-thick layers, and (b, c) the corresponding schematic atomic models, clearly showing distinct atomic configuration corresponding to hexagonal Co and cubic Co₃O₄.

state that it is a very active catalyst” and “I believe that this manuscript may cause many to re-think the accepted strategies for the electroreduction of CO₂”.

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