

CoMo Nanoclusters Supported on Atomically Dispersed Co and Mo Active Sites for Hydrogen Evolution Reaction

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Introduction

Anthropogenic carbon emissions have led to a 1.1°C increase in global temperatures with reference to the pre-industrial level, which was mainly due to the combustion of fossil fuels. Hydrogen is a clean energy carrier, which could be the answer to this problem since it produces zero carbon emissions, and electricity, water, and heat are its only products when it is used in fuel cells. To meet with hydrogen economy era, society needs to solve several technical challenges urgently, i.e., production, transportation, and storage of hydrogen. Hydrogen production remains the biggest hurdle in sustainably closing the hydrogen cycle. As of 2021, the world's hydrogen productions are mainly carried out by thermochemical methods. To eliminate the depletion of fossil fuel resources, using water resources could be the key to keeping the global temperature increase to within 1.5°C. However, water electrolysis processes have long been criticized for their general sluggish rate, high electricity consumption, and the use of expensive platinum (Pt) electrodes, making them not practical for commercial use. Therefore, reducing overpotentials and replacing the uses of Pt with other more economically viable metals become effective strategies for driving the green hydrogen energy transition.

Technical Challenge

The best record to use non-Pt-based electrodes for hydrogen evolution reaction (HER) from water electrolysis is the Ru NPs supported on 2D nitrogen-doped carbon structure, with an overpotential of 17 mV at 10 mA/cm². However, due to technical bottlenecks such as high cost, scarcity, and limited stability, there is still a long way to go toward commercialization. Base metal catalysts such as Cu, Co, Mo, Fe, and Ni are more economically viable but they generally exhibit much lower stability and sluggish reaction rates. Recent strategies to increase the intrinsic activity of active sites include 1) downsizing the nanoparticle catalysts (NPs) to increase the surface area and the number of active sites such as single atom catalysts or atomically dispersed sites on carbon supports, and 2) creating dual-active sites for water dissociation and surface for H_{ads} adsorption, respectively. However, so far no clear correlation between size and reactivity for NPs has been found. For example, in acidic media, while Pt_{nano} with 230 nm showed excellent HER activity, Pt₁₀ monodisperse nano-clusters showed only much reduced catalytic activity. Clearly, the HER performance cannot be boosted by just one single size factor but may require multiple strategies.

Objectives

This study explores the synergistic effects between the Co and another non-precious metal, with the presence of nanoparticles (NPs) and single atoms (SAs) for the hydrogen evolution reaction in alkaline media. In addition, it aims to determine the physicochemical properties and evaluate the heterogeneous catalytic H₂ production performance for a better understanding of the correlation between unique electronic structures and catalytic performance.

Results

Interestingly, we have recently developed a type of catalyst that can increase the atom utilization. Our recent preliminary studies found that non-precious downsized metal catalysts Co supported on carbon nanotube (CNT) with atomically dispersed CoN₄ demonstrated an overpotential of 155 mV at a current density of 10 mA/cm² with a Tafel slope of 152.05 mV/dec, which showed a great improvement than regular Co NPs supported on N-doped carbon ($\eta_{10} = 337$ mV). And when pairing up with Mo metal, bimetallic CoMo supported on CoMoN₆-CNT demonstrated an even lower overpotential of 130 mV at a current density of 10 mA/cm² and a Tafel slope of 156.08 mV/dec (Figure 1). The improved performances could be due to the presence of atomically dispersed dual-metal active sites on the catalyst support.

In addition, DFT studies on the adsorption behaviors of H₂O molecules on atomically dispersed CoMo dual-active sites on carbon materials were also performed for the Volmer and the Tafel steps under alkaline media to elucidate the electrocatalytic process for H₂O splitting. We calculated the optimized structures and the free energies of the HER.

As shown in Figure 2a, the low value of $\Delta G_{\text{H}_2\text{O}}$ (more negative) of the H₂O adsorption on MoN₄ surface indicates the strong binding of H₂O on the catalyst surface, while the high $\Delta G_{\text{H}_2\text{O}}$ value of the H₂O adsorption on CoN₄ surface indicates a weak binding.

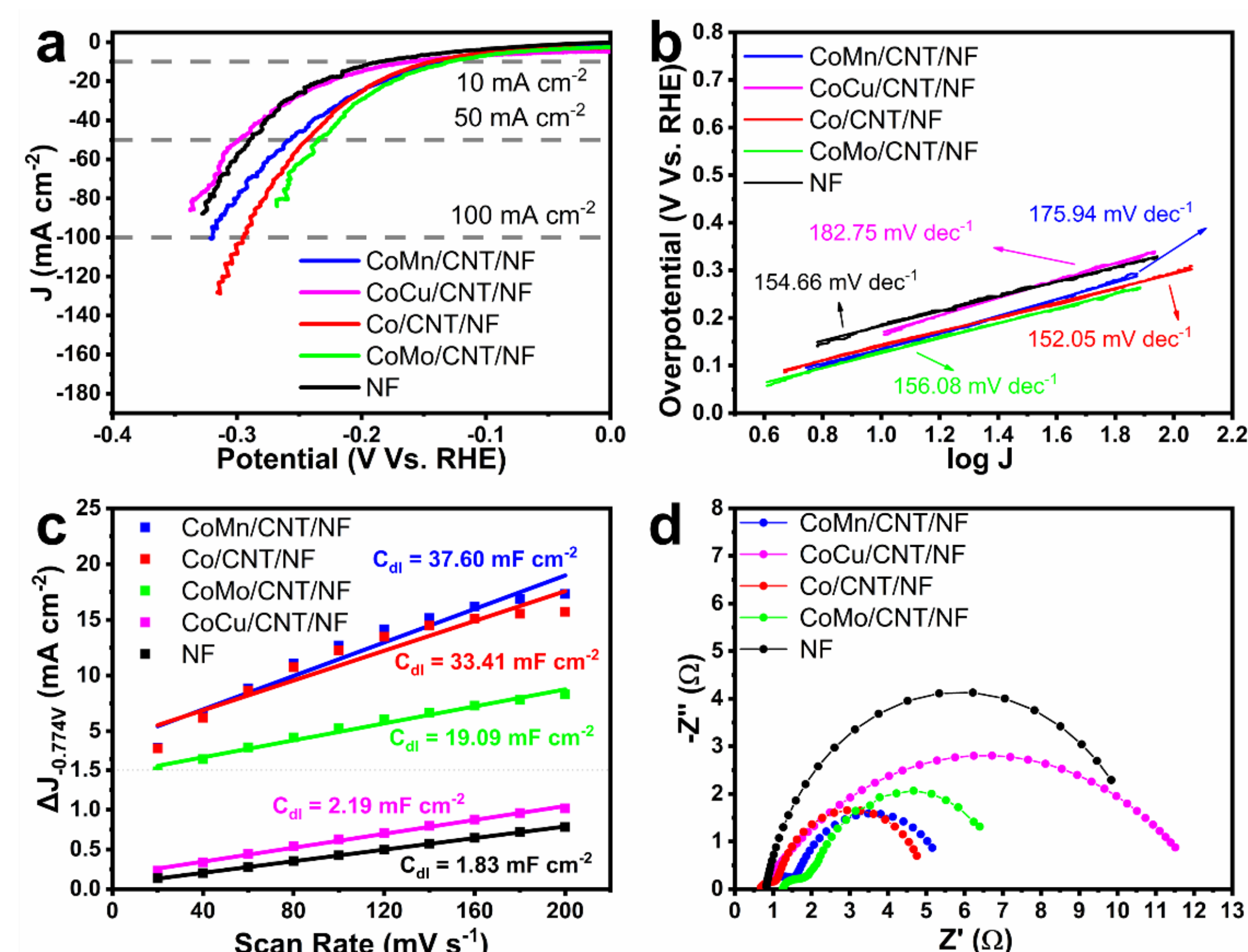


Figure 1 (a) HER polarization curves of electrocatalysts, (b) the corresponding Tafel plots for different electrocatalysts, (c) the measured capacitive current density at -0.774 V vs. Hg/HgO as a function of the scan rate, used to indicate the electrochemically effective active surface area, (d) Nyquist plots of the different electrocatalysts at an overpotential of 200 mV. The fitted curves are presented by solid lines.

Doping the Mo with Co results in a more optimal adsorption of H₂O on the Mo center (0.04 eV), which is also validated by the shorter bond length of the H₂O-Mo bond (Figure 2d) compared with H₂O-Co bond (Figure 2c). As shown in Figure 2b, the adsorption of H also shows that the optimal ΔG_{H} is on the Mo center of the dual-atom catalysts (0.23 eV), which may explain the better performance of the above preliminary experimental studies. The longer distance between H and Mo in Figure 2f also indicates a more facile recombination of two H_{ads} to form the H₂ molecule. PDOS studies showed that after Co is paired up with Mo, the up-spin and down-spin showed an upshift and downshift, respectively, both closer to the Fermi level. Thus, Co and Mo can synergistically boost HER activity. The free energy of the Heyrovsky step is yet to be studied, but it is highly probable that the reaction is Volmer-limiting due to the relatively large Tafel slope.

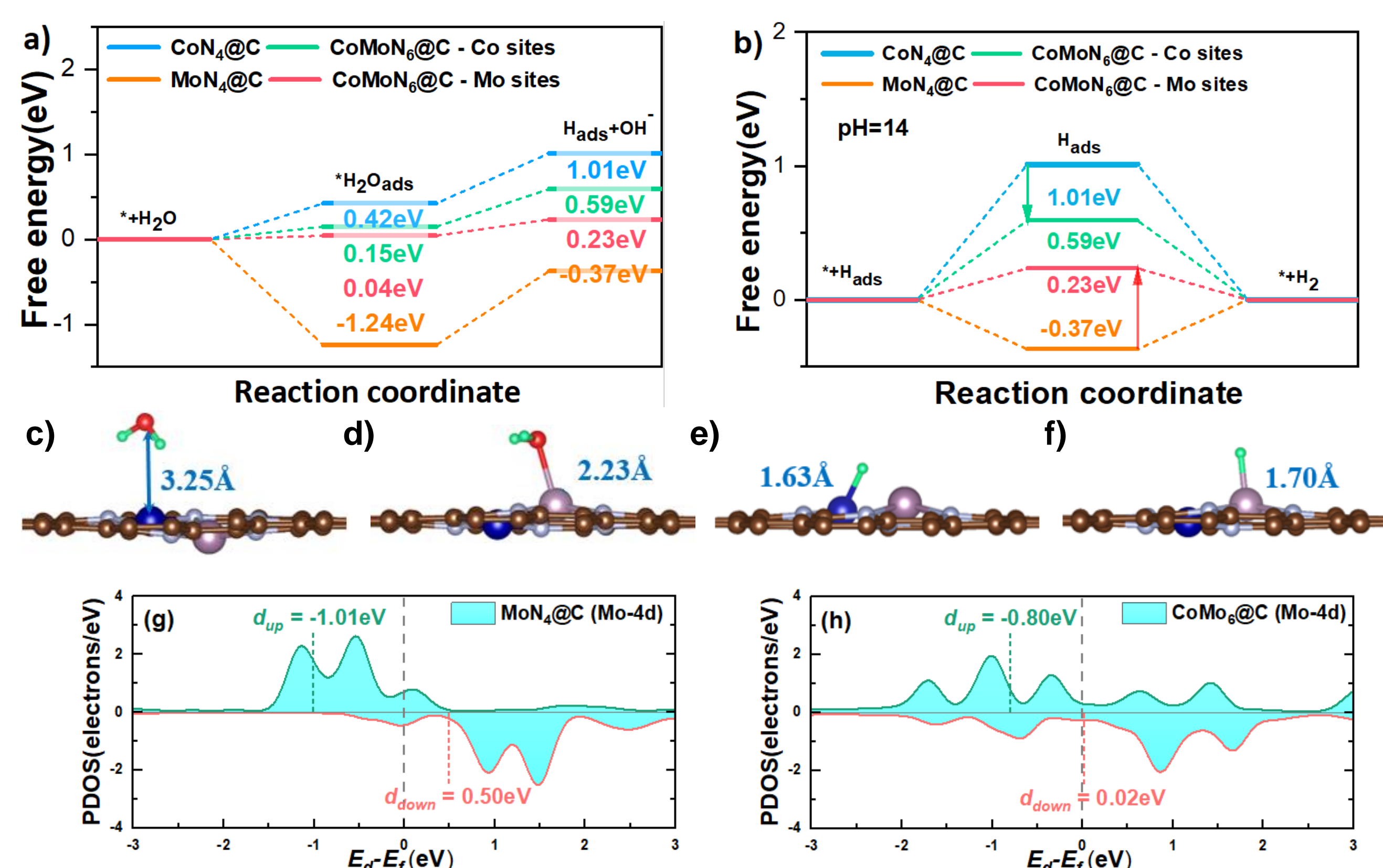


Figure 2 a) the Volmer step for catalysts with single and dual-active sites; b) the Tafel step for catalysts with single and dual-active sites; c - f) optimized structures of H₂O and H adsorbed species on Co and Mo centers of the catalysts; g - h) PDOS of MoN₄ and CoMoN₆ on carbon materials, where E_d = d-band center, E_f = Fermi level.

Conclusion

The improved performances could be due to the presence of atomically dispersed dual-metal active sites on the catalyst support. Thus, a much more precise synthesis of the catalysts to increase the number of pair-sites could result in much better outcomes. In addition, by modulating the coordination environment of the dual-metal sites with the appropriate combination of non-metal atoms, together with interfacial engineering of the one-dimensional catalytic materials, both the reactivity and stability can further be enhanced.