Electronic Supplementary Information

The metal-support interactions of $Cr(OH)_3$ enhance the performance of supported Au-based benzyl alcohol electrooxidation catalysts†

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Materials: Chromium trichloride ($CrCl_3$, 95%, Macklin), in-dodecanethiol (99.5%, Aladdin), cetyltrimethylammonium chloride (CTAC, 97%, Aladdin), potassium hydroxide (KOH, 99.999%, Aladdin), Benzyl alcohol (99.9%, Aladdin), ethylene glycol (99.9%, Aladdin), Ethanol (EtOH, 99.9%, Aladdin), chloroauric acid ($HAuCl_4 \cdot 4H_2O$, Sinopharm Chemical Reagent Co. Ltd), copper(II) potassium hydroxide (KOH, 99.999%, Aladdin), All reagents are used as received without further purification.

$Cr(OH)_3$ Synthesis: 500 mg of $CrCl_3$, 3 pieces of Ni foam(1*2.5 cm^2) and 200 mg of urea were mixed with 28 mL of H_2O. The solution was then transferred to a 50-mL Teflon-lined stainless steel autoclave, sealed, placed in an oven. It was heated to 165 °C and maintained at this temperature for 12 h. After cleaning with ethanol and water, dry at 50°C for 2 h. $Cr(OH)_3$ support can be available.

Au-$Cr(OH)_3$ Synthesis: Add 20 mg $HAuCl_4$ $4H_2O$ to 15 mL glycol. Ultrasonic to uniform dispersion and then add the prepared $Cr(OH)_3$ support. The reaction was carried out in N_2 atmosphere at 80°C for 1 h. Wash with ethanol and water and dry. And you get Au-$Cr(OH)_3$.

Au/C Synthesis: In the typical synthesis of Au NPs, 20 mg $HAuCl_4$ $4H_2O$ were prepared by mixing 13.5 mL of ethylene glycol, and 60 mg CTAC in a three flask. The solution was then heated to 160 °C under Ar atmosphere with stirring for 30 min. The Au NPs were finally collected by centrifugation with the addition of EtOH, and redispersed in 1.0 mL of EtOH.

20 mg high surface area carbon (Vulcan XC-72, Carbon) was dispersed in 5 mL of cyclohexane. Then the as-prepared Au/C were added dropwise to the dispersion. The mixture was magnetically stirred for 10 h, and the carbon-supported catalysts were collected by filtration.

Physical Characterization: The XRD patterns were obtained on a Rigaku D/Max 2500 VB2+/PC X-ray powder diffractometer equipped with Cu Kα radiation ($\lambda = 0.154$ nm) operating at 40 kV and 40 mA. All of the diffraction data were collected at a scanning rate of 10° min^{-1}. The TEM images were conducted by a HITACHI HT7700 transmission electron microscope. The HRTEM image, EDS mapping, and EDS line scanning were performed on a JEOL JEM-2010F transmission electron microscope. The XPS spectra were recorded on a Thermo Fisher ESCALAB 250Xi XPS system with a monochromatic Al Kα X-ray source. The binding energies derived from XPS measurements were calibrated to the C 1s at 284.8 eV.

Electrochemical Measurements: The electrochemical measurements were operated in a three-electrode system controlled by a potentiostat (Bio-logic). The electrolytes for the BAOR were 1.0 M KOH and 0.1 M Benzyl alcohol. The catalyst ink was prepared by dispersing 2 mg of catalyst in the mixed solution of isopropanol (740 μL), water (240 μL), and Nafion solution (20 μL, Alfa Acesar, 5 wt%). The Au/C ink were drop on a Ni foam electrode and used as the working electrode. In order to ensure the reliability of the test activity, all the tests were conducted in Ar atmosphere at 30 °C.

Computational method: We have employed the Vienna Ab initio Simulation Package (VASP)to perform all density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Revised Perdew-Burke-Ernzerhof (r-PBE)functional. We have chosen the projected augmented wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV. The DFT-D3 empirical correction method was employed to describe van der Waals interactions. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. Monkhorst-Pack k-points of 1×1×1 was applied for all the calculations. Half atoms at bottom are fixed in all the calculations. The Gibbs free energy was calculated by the following equation:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

Where the value of ΔE, ΔE_{ZPE} and ΔS denotes the changes of DFT energy, the zero-point energy and the entropy at 298.15K, respective.

Based on the characterization results of $Cr(OH)_3$, we fixed the bottom half of $Cr(OH)_3$ to simulate a support with a certain thickness. The $Cr(OH)_3$ of the upper layer and the loaded Au atom were optimized, and the influence of the interface on the structure was also considered. At the same time, we also carried out structural optimization based on the results of HRTEM.

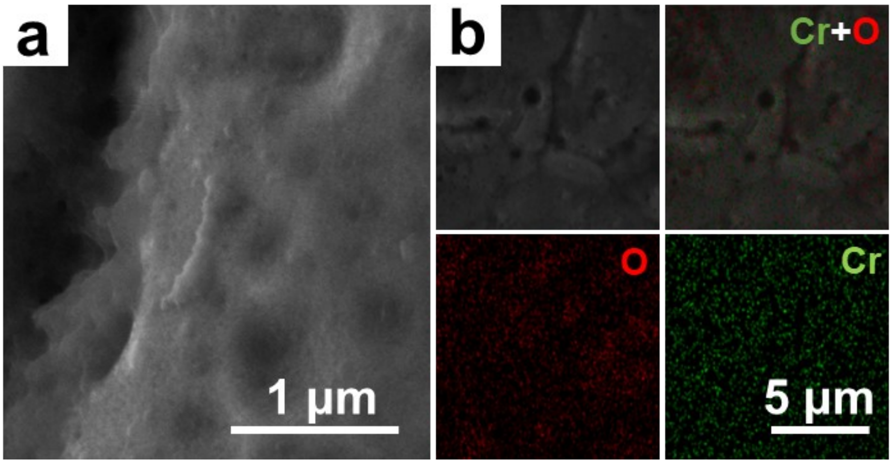

Fig. S1. SEM image of $Cr(OH)_3$.

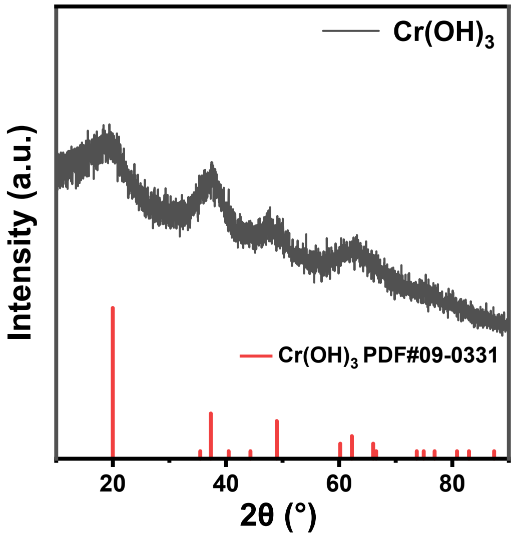

Fig. S2. XRD Patterns of Cr(OH)$_3$.

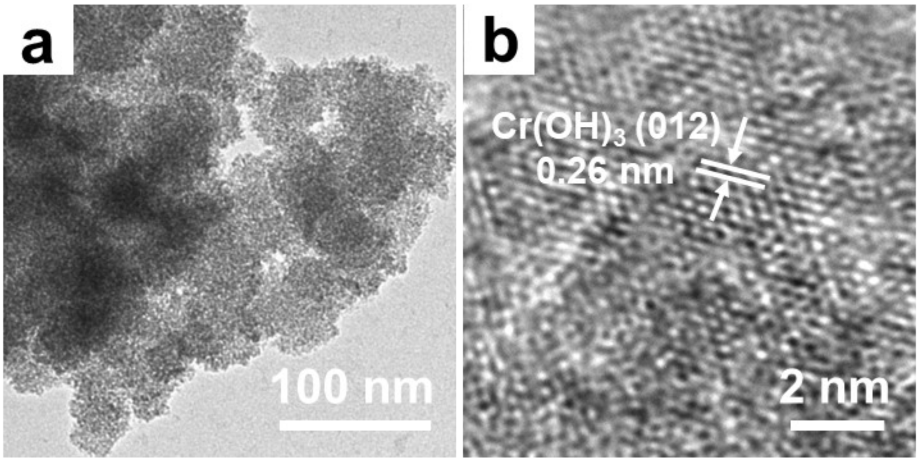

Fig. S3. (a) TEM and (b) HRTEM image of $Cr(OH)_3$.

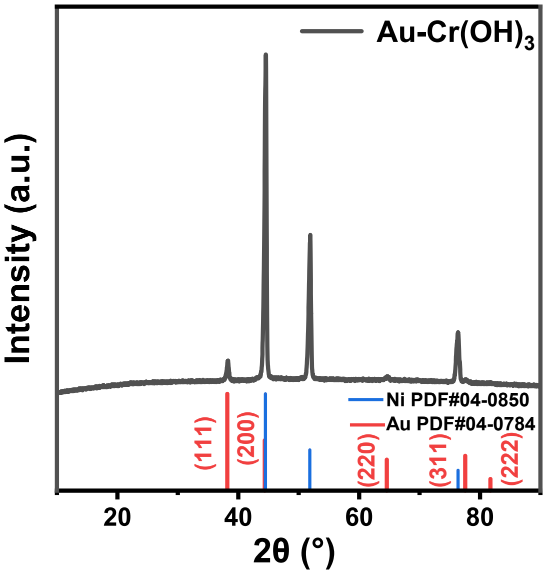

Fig. S4. XRD Patterns of Au-Cr(OH)$_3$.

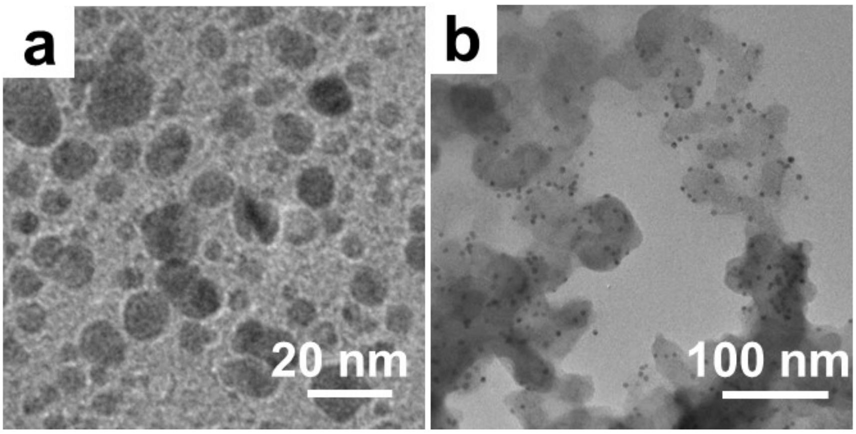

Fig. S5. TEM image of (a) Au NPs and (b) Au/C (Au NPs supported on Volcan C).

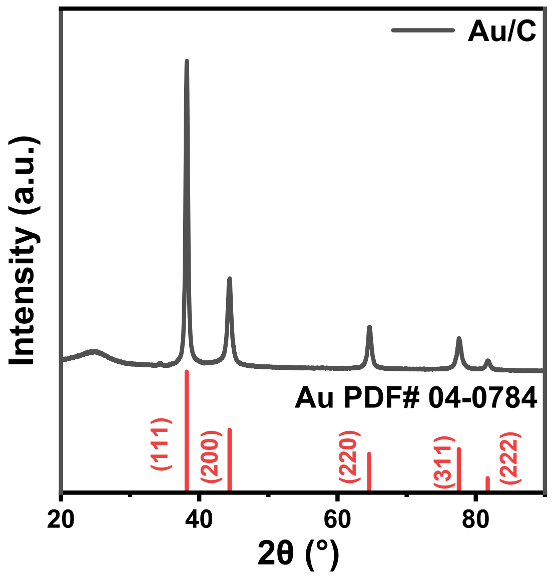

Fig. S6. XRD Patterns of Au/C.

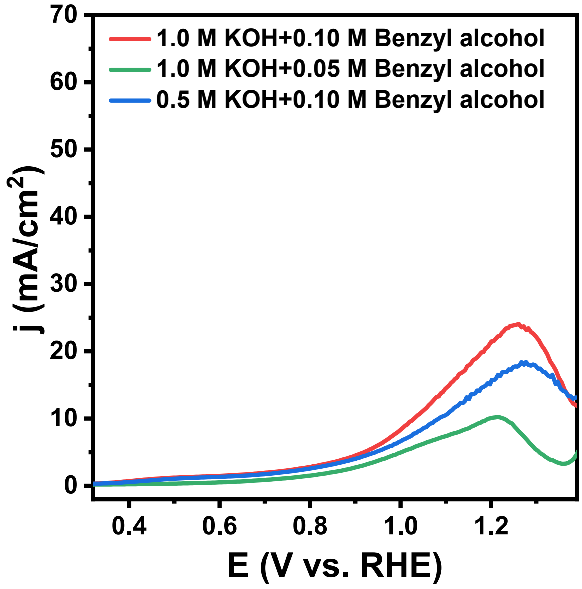

Fig. S7. Polarization curves of Au/C in different electrolytes.

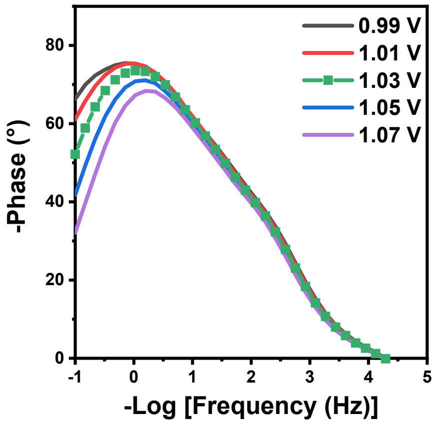

Fig. S8 Bode plots of the $Cr(OH)_3$ in 1.0 M KOH with 0.1 M benzyl alcohol

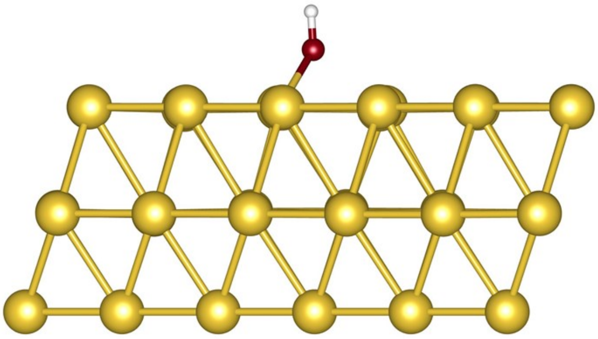

Fig. S9. DFT-Calculation model of OH^- adsorption on Au/C.

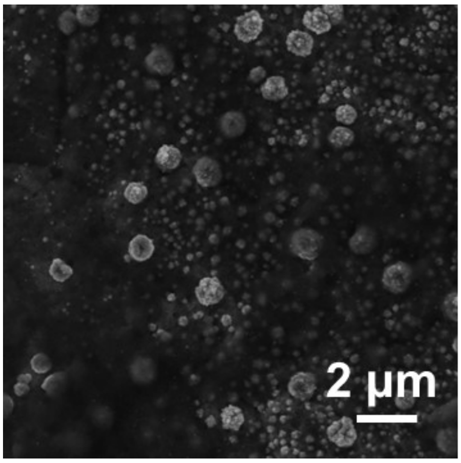

Fig. S10. SEM image of Au-$Cr(OH)_3$ after BAOR.

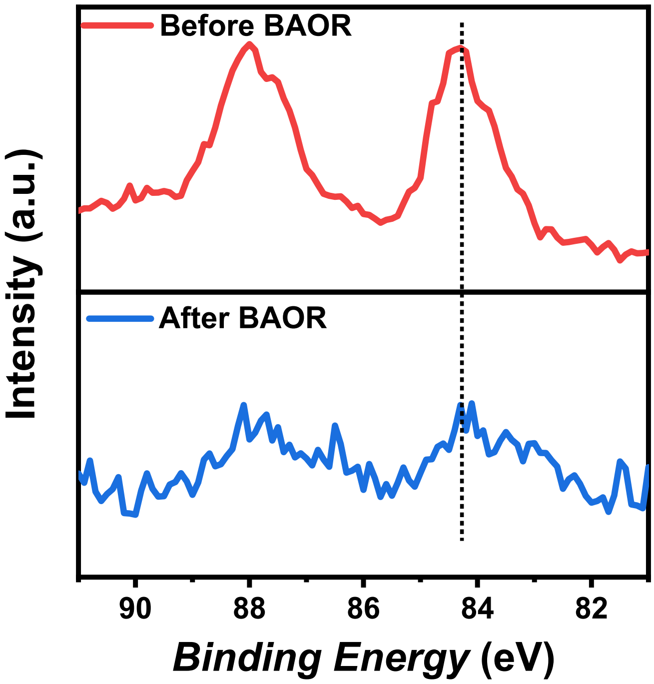

Fig. S11. XPS spectra of Au in Au-$Cr(OH)_3$ before and after BAOR.