Supplementary Information for
Dynamic transformation between bilayer islands and dinuclear clusters of Cr oxide on Au(111) through environment and interface effects

Zhiyu Yi\textsuperscript{a,b,1}, Le Lin\textsuperscript{a,c,1}, Yuan Chang\textsuperscript{d}, Xuda Luo\textsuperscript{a,b}, Junfeng Gao\textsuperscript{d}, Rentao Mu\textsuperscript{a}, Yanxiao Ning\textsuperscript{a,2}, Qiang Fu\textsuperscript{a,e,2}, and Xinhe Bao\textsuperscript{a,e,2}

\textsuperscript{a}State Key Laboratory of Catalysis, iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; \textsuperscript{b}University of Chinese Academy of Sciences, Beijing 100049, China; \textsuperscript{c}School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China; \textsuperscript{d}Key laboratory of Material Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian, 116024, China; \textsuperscript{e}Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; \textsuperscript{1}Z.Y. and L.L. contributed equally to this work. \textsuperscript{2}To whom correspondence may be addressed. Email: yxning@dicp.ac.cn; qfu@dicp.ac.cn; or xhbao@dicp.ac.cn.

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Supplementary Information Text

Experimental section

Different methods for growing CrO$_2$-bilayer(BL) nanoislands.

The CrO$_2$-BL nanoislands shown in the main text were prepared by evaporation of metallic Cr in UHV and post-annealing in O$_2$. In the O$_2$ atmosphere ranged from $1 \times 10^{-7}$ to $5 \times 10^{-6}$ mbar and with the annealing temperatures from 500 to 650 K, the synthesized nanostructure was CrO$_2$-BL nanoislands. While in low O$_2$ oxygen regime ($5 \times 10^{-8}$ mbar), the CrO$_x$ prepared was not so flat, and there existed many irregular structures in the boundary of islands (Fig. S8A). Another method was also performed to grow CrO$_x$, i.e., reactive deposition in O$_2$ followed by annealing in UHV (Fig. S9A), which also formed CrO$_2$-BL nanoislands.

Different methods for growing Cr$_2$O$_7$ clusters.

Different growth methods also resulted in the formation of Cr$_2$O$_7$-dinuclear clusters. If post-annealing the Cr/Au(111) surface in $5 \times 10^{-8}$ mbar O$_3$ at 440 K, the same Cr$_2$O$_7$-dinuclear clusters were formed (Fig. S10A). Another growth process was deposition of Cr on O$_3$ pre-adsorbed Au(111) surface at RT and annealing in UHV, producing the same clusters with low coverage (Fig. S10B). The annealing temperature is quite critical. If lower than 420 K, the atomic oxygen on Au cannot desorb. If higher than 480 K, the Cr$_2$O$_7$ clusters and CrO$_2$-BL nanoislands will co-exist on the surface.

Theoretical section

Hubbard U correction

To reach accurate energetics, the generalized gradient approach (GGA)+U methods need to be used for the chromium oxides, e.g., CrO$_3$ (Ama2, no. 40) and Cr$_2$O$_3$ ($R\bar{3}c$, no. 167). According to the standard formation enthalpy ($\Delta_{rxn}H = -0.82$ eV) of the reaction $2\text{Cr}_2\text{O}_3 + 3\text{O}_2(g) \rightarrow 4\text{CrO}_3$ (1, 2), we find that an effective Hubbard $U$ ($U_{\text{eff}} \approx -2.5$ eV) is suitable for characterizing on-site Coulomb repulsion between $3d$ electrons of the oxidative Cr. Here, the total energy of O$_2$ molecule is corrected using the water reference scheme (3) and is 9.46 eV within the GGA+D3 calculation (4). We then obtain the corrected energy (-7.72 eV) of metallic Cr by preserving the reaction enthalpy ($\Delta_{rxn}H = -23.52$ eV) of $4\text{Cr} + 3\text{O}_2(g) \rightarrow 2\text{CrO}_3$, which nearly amounts to the energy per Cr atom of bulk Cr ($Im\bar{3}m$, no. 229) with $U_{\text{eff}} \approx -1.8$ eV correction.

Ab initio molecular dynamics (AIMD)

AIMD simulations through using VASP are performed to estimate the stability of the Au(111)-supported CrO$_x$ film (at 610 K) and cluster (at 440 K) series. The NVT ensemble is used within a Nosé-Hoover thermostat, and the durations of these simulations are 5 or 10 ps for reaching the equilibrium simulation with a time step of 1 fs (5).

Model constructions

We optimized the lattice constants of the used Au(111) and free-standing (FS) CrO$_x$ films, which are 2.91 Å for Au(111), 6.12 Å for FS Cr$_2$O$_3$-ML, and 5.65 Å for FS CrO$_2$-BL (Fig. S12). The CrO$_x$/Au(111) interfaces are constructed through adjusting the lattices of the FS CrO$_x$ films to fit the Au(111) lattice, where the mismatches are 3.52% for the Cr$_2$O$_3$-ML and 7.08% for the CrO$_2$-BL. Notably, choosing the large mismatch between Au(111) and CrO$_2$-BL is because that the CrO$_2$-BL inclines to relax into the 12-membered-
ring geometry (Fig. S2) from a contractive structure (Fig. S12). We thus obtain four sets of moiré patterns of the CrO$_2$/Au(111) heterointerfaces, i.e., Cr$_2$O$_3$-ML-(5 × 5)/Au(111)-(√19 × √19) and CrO$_2$-BL-(√3 × √3)/Au(111)-(√13 × √13), as well as the derived Cr$_2$O$_3$-BL-(5 × 5)/Au(111)-(√19 × √19) and Cr$_2$O$_3$-ML-(√3 × √3)/Au(111)-(√13 × √13) in Fig. S2. For the clusters on Au(111), we adopt a (5 × 5)-Au(111) supercell with a four-atomic-layer slab as the substrate, where only the bottom two layers are constrained as the bulk. Within the Monkhorst-Pack scheme, we sample the k-point grids ($k_a$) to maintain the product of $k_a^*a > 25$ for oxides and $k_a^*a > 35$ for metals. Here, we use the k-points of (3 × 3 × 1) for the (5 × 5) and (√19 × √19) supercells, and (4 × 4 × 1) for the (√13 × √13) supercells.

**Formulae**

(1) Energy levels of the states were corrected to the Gibbs free energies by

$$G_{\text{adsorbate}} = E_{\text{elec}} + ZPE + \delta H - T\Delta S$$

(1.1)

$$\mu_{\text{gas}} = E_{\text{elec}} + ZPE + \delta H - T\Delta S + k_BT\ln \frac{p_{\text{gas}}}{p^o}$$

(1.2)

where $E_{\text{elec}}$ is the electronic energy calculated by DFT at 0 K, $ZPE$ is the zero point energy, $\delta H$ is the integral of heat capacity, and $T\Delta S$ is the energy of entropy change ($T$ is the absolute temperature). For the adsorbed species ($G_{\text{adsorbate}}$), the last three items were obtained by vibrational frequency calculations via the standard methods. For the gaseous species ($\mu_{\text{gas}}$), the corrections were taken from the NIST database through standard ideal-gas method and with consideration of the partial pressure of the gas ($p_{\text{gas}}$) (1, 3, 6, 7). The relevant values were addressed via the VASPKit code which uniformly regards the frequency of <50 cm$^{-1}$ as 50 cm$^{-1}$.

(2) The formation energy of the free-standing Cr$_x$O$_y$ nanostructures ($E_{\text{form\_film or cluster}}$) and the interface ($E_{\text{form\_interface}}$):

$$E_{\text{form\_film (or cluster)}} = \frac{1}{x}(E_{\text{Cr}_x\text{O}_y} - xE_{\text{Cr}} - \frac{y}{2}E_{\text{O}_2})$$

(2.1)

$$E_{\text{form\_interface}} = \frac{1}{x}(E_{\text{Cr}_x\text{O}_y/Au(111)} - E_{\text{Au(111)}} - xE_{\text{Cr}} - \frac{y}{2}E_{\text{O}_2})$$

(2.2)

where $E_{\text{Cr}_x\text{O}_y}$, $E_{\text{Cr}_x\text{O}_y/Au(111)}$, $E_{\text{Au(111)}}$, $E_{\text{Cr}}$, and $E_{\text{O}_2}$ are the total energies of the free-standing Cr$_x$O$_y$, the Cr$_x$O$_y$/Au(111), the Au(111) substrate, the bulk Cr (per Cr atom), and the gaseous O$_2$ molecule, respectively. $x$ and $y$ are the numbers of Cr and O atoms in the Cr$_x$O$_y$ formation. Here, the high-accurate water reference scheme is used to correct the total energy of O$_2$ (due to its overbinding (9)) through preserving the reaction energy of H$_2$(g) + 0.5O$_2$(g) $\rightarrow$ H$_2$O(g) (3).

(3) The interface adhesion energy ($E_{\text{adh}}$) exerted by Au(111) to make the Cr$_x$O$_y$ nanostructures adhering on it,

$$E_{\text{adh}} = \frac{1}{x}(E_{\text{Cr}_x\text{O}_y/Au(111)} - E_{\text{Au(111)}} - E_{\text{Cr}_x\text{O}_y})$$

(3)

(4) The Gibbs free energy of formation of Cr$_x$O$_y$ films or clusters ($\Delta G$):

$$\Delta G = \frac{1}{x}(E_{\text{Cr}_x\text{O}_y/Au(111)} - E_{\text{Au(111)}} - xE_{\text{Cr}} - y\mu_0)$$

(4.1)

$$\mu_0 = \frac{1}{2}\left(E_{\text{O}_2} - T\Delta S + k_BT\ln \frac{p_{\text{O}_2}}{p^o}\right)$$

(4.2)
where $\mu_0$ is the chemical potential of O atom referenced to the O$_2$ at given temperature ($T$) and pressure ($p_{O_2}$) and is corrected by the method by Zeng et al (3). Notably, we prescribe $\Delta \mu_O = \mu_O - \frac{1}{2} E_{O_2}$ which is used as the $x$ coordinates in phase diagram (10).

**Fig. S1.** XPS O 1s spectra corresponding to Cr 2p shown in (A) Fig. 1E, (B) Fig. 2E, (C) Fig. 3B, (D) Fig. 4D, (E) Fig. 4H of the main text. A small number of hydroxyl-related species (peak at 532 eV) shown in O 1s spectra may come from the weak surface hydroxylation by H or H$_2$O species from the UHV background. The brighter clusters at the boundary of nanoislands are observed in the high-resolution STM images of CrO$_2$-BL nanoislands (SI Appendix, Fig. S13), which could be the -OH groups. The O/Cr ratio can be calculated by using peak areas of XPS O 1s and Cr 2p, which is a semiquantitative analysis.
Fig. S2. Configurations (top and side views) and simulated STM images (the bottom row) of the proposed four films, including Cr$_2$O$_3$-monolayer (ML) and bilayer (BL), Cr$_2$O$_5$-ML, and CrO$_2$-BL on Au(111). The numbers mark the height in Å of the topmost Cr layer away from the Au surface. Additionally for CrO$_2$-BL/Au(111), the interface distance between the bottom Cr layer and the Au surface and its polyhedral view are shown. O: red; Cr: green; Au: golden.
**Fig. S3.** Final configurations of the Au-supported CrO$_x$ films after over the AIMD simulation at 610 K. The simulation time is given in each column. O: red; Cr: green; Au: golden.
**Fig. S4.** Analyses of the geometric and electronic structures for the bulk Cr$_2$O$_3$ and CrO$_3$, the CrO$_2$-BL film and z-Cr$_2$O$_7$ cluster on Au(111). (A) Configurations of the bulk Cr$_2$O$_3$ and CrO$_3$, CrO$_2$-BL film, and z-Cr$_2$O$_7$ cluster on Au(111). The characteristic O atoms are divided into three types, including the bridged O$_{bri}$, dangling O$_{dan}$, and interfacial O$_{int}$. O: red; Cr: green; Au: golden. (B and C) Projected density of states (PDOS) of the Cr (B) and O (C) atoms in the bulk Cr$_2$O$_3$ and CrO$_3$, CrO$_2$-BL film and z-Cr$_2$O$_7$ cluster on Au(111). (D) PDOS for three types of O atoms in the Cr$_2$O$_7$ cluster on Au(111), including the O$_{int}$, O$_{bri}$, and O$_{dan}$. The light green blocks highlight the DOS difference around the Fermi level.
**Fig. S5.** STM images of (A) isolated Cr$_2$O$_7$-dinuclear clusters (0.03 ML) grown on Au(111) by Cr deposition in UHV, O$_3$ dose at RT and UHV annealing at 440 K (50 × 50 nm$^2$; I = 0.3 nA, bias = 0.1 V); (B) Cr$_2$O$_7$-dinuclear clusters (0.45 ML) grown on Au(111) (50 × 50 nm$^2$; I = 0.1 nA, bias = 0.3 V).
Fig. S6. Configurations and simulated STM images of the CrO$_x$ clusters on Au(111) with coordinatively unsaturated (A) and saturated (B) Cr atoms. The CrO$_3$, Cr$_2$O$_5$, Cr$_2$O$_6$, Cr$_3$O$_7$, CrO$_4$, Cr$_2$O$_7$, Cr$_3$O$_{10}$, and Cr$_4$O$_{13}$ in stoichiometry are included. O: red; Cr: green; Au: golden. Here, the distances of Cr-Cr (black D$_{Cr-Cr}$) and of the bright dots (white D$_{dots}$) are marked.
Fig. S7. The nature of stability difference of the clusters: Au(111)-supported vs. free-standing (FS). (A and B) Phase diagrams of the Au-supported and FS clusters with different Cr+O stoichiometries at 440 K and variable O$_2$ pressures. (C) Configurations of the FS CrO$_x$ clusters with coordinatively saturated Cr (green) atoms. The characteristic O atoms (red) are highlighted, including the dangling O$_{dan}$ and bridged O$_{bri}$. (D) Percentages of the characteristic O atoms in the FS CrO$_x$ clusters.
**Fig. S8.** STM images of CrO$_x$ islands grown on Au(111) by Cr evaporation in UHV followed by annealing in oxygen at different pressures: (A) $5 \times 10^{-8}$ mbar O$_2$ (50 $\times$ 50 nm$^2$; I = 0.1 nA, bias = 1.0 V); (B) $5 \times 10^{-6}$ mbar O$_2$ (50 $\times$ 50 nm$^2$; I = 0.1 nA, bias = 1.0 V).
Fig. S9. (A) STM images of CrO$_2$-BL nanoislands grown on Au(111) by deposition in $5 \times 10^{-7}$ mbar O$_2$ at 180 K and annealing in UHV at 610 K (50 $\times$ 50 nm$^2$; I = 0.1 nA, bias = 1.0 V). (B) Same diagram as (A) with different color scale to show the herringbone reconstruction on the open Au surface.
**Fig. S10.** STM images of Cr$_2$O$_7$-dinuclear clusters grown on Au(111) by different methods: (A) deposition in UHV and annealing in O$_3$ at 440 K (50 × 50 nm$^2$; I = 0.1 nA, bias = 1 V); (B) O$_3$ pre-dosing at RT, Cr deposition in UHV and UHV annealing at 440 K (50 × 50 nm$^2$; I = 2.0 nA, bias = 0.1 V).
**Fig. S11.** STM images of (A) Au(111) exposed to $5 \times 10^{-8}$ mbar O$_3$ at RT (45 × 45 nm$^2$; I = 0.1 nA, bias = 1.0 V); (B) the sample of (A) exposed to $5 \times 10^{-8}$ mbar CO at RT (50 × 50 nm$^2$; I = 0.1 nA, bias = 1.0 V).
**Fig. S12.** The used free-standing $\text{Cr}_2\text{O}_3$-ML (A) and $\text{CrO}_2$-BL (B) films (side and top views). (C) The extended $\text{CrO}_2$-BL model (left) and its simulated STM image (right). O: red; Cr: green.
Fig. S13. STM images of (A) Same area as Fig. 1B; (B) the red square area in (A) (12 × 12 nm²; I = 0.1 nA, bias = 1.0 V); (C) the atomically resolved STM image of the nanoisland in (B) (12 × 12 nm²; I = 0.1 nA, bias = 0.3 V). The bright clusters at the boundary could be the -OH groups.

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