Supporting Information

K atom promotion of O_2 chemisorption on Au(111) Surface

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I. dI/dV spectra of clean Au(111) and K/Au(111)

Figure S1 shows the typical spectra performed on Au(111) and K/Au(111) surfaces. The sharp step-shaped onset of Au(111) surface state at -0.48 V can be clearly seen in the black line. Unlike the symmetric peaks with respect to the Fermi energy taken of K_2O_2 dots, the spectrum taken of K/Au(111) surface is featureless.

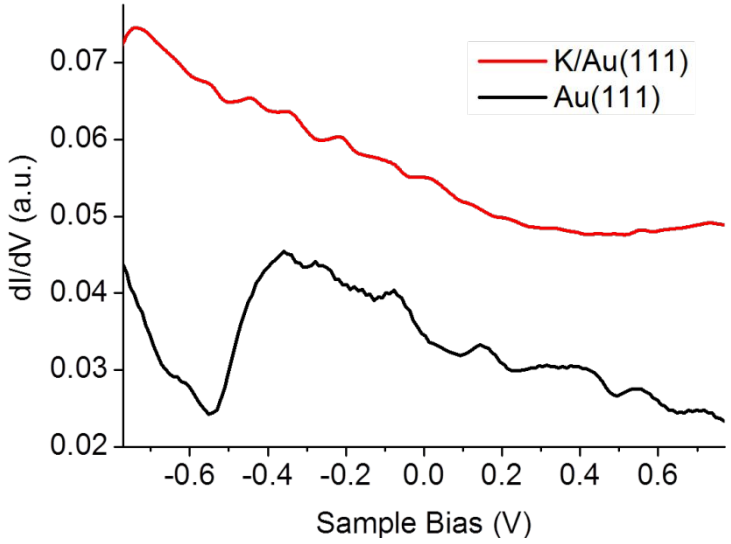
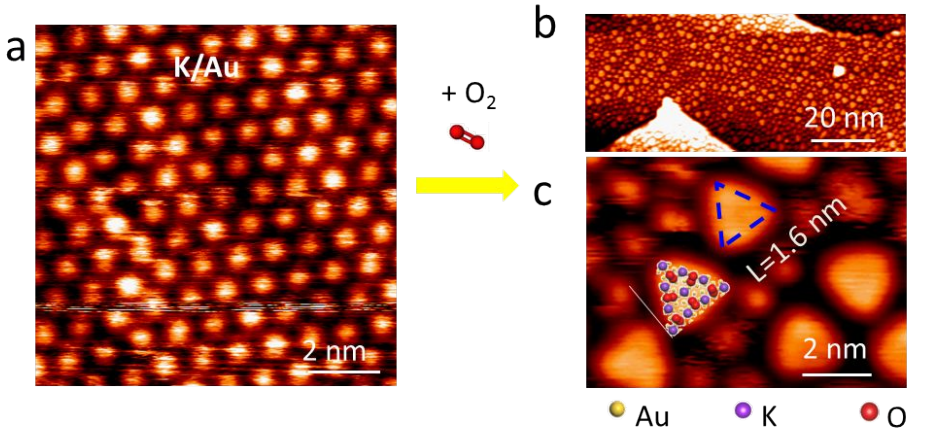


Figure S1 . *dI/dV* spectra measured on Au(111) (black line) and K/Au(111) (red line). The red curves have been shifted vertically for clarity, T = 4.5 K, tunnelling parameters: I = -0.1 nA, V_b = -0.4 V.

II. Estimation of the number of K atoms within in each triangular island

Figure S2b is a topographic image of O-K/Au(111) surface after dosing of O_2 on intermediate K coverage sample. To estimate the precisely the number of K atoms contained in each triangular island, we perform a statistical analysis of the number of K atoms before the O_2 dosing and the K_2O_2 dots and K-O triangular islands (after the dosing process) based on counting several thousands of atoms/clusters in 30 × 30nm STM images (Figure S2d). Based on such counting, assuming that each K_2O_2 dot has taken two K atoms, to account for all of the initially present K atoms we conclude that each triangular island should on average contain ten K atoms. According to DFT calculations, stable K-O_2 structure containing ten K atoms, and forming stable equilateral triangle structures with 1.6 nm sides is superimposed on the image of a triangular island in Figure S2c.



d

K/Au(111)	O-K/Au(111)	
K atoms	K_2O_2	K-O_2 triangular islands
10810	2637	659

Figure S2. (a) STM image of K atoms on Au (111) before dosing of O_2. (b) Large scale STM image of O-K/Au surface after exposing (a) to oxygen. (c) The most probable K-O_2 triangle structure calculated by DFT that accounts for the K atom number and triangle geometry and size is displayed. (d) Estimated distribution of K before and after O_2 dosing.

III. O_2 dosing and temperature dependence measurements

We also tested the effect of further dosing of O_2 molecules on K-O_2 sample. We first recorded an image after the initial O_2 dosing, then retracted STM tip far away from the sample surface so that the tip does not affect the local O_2 adsorption. After dosing of additional 1 L of O_2 molecules the structure the distribution of K−O_2 complexes did not change when rescanning the same area in Figure S3a and S3b.

Moreover, to determine the stability of K_2O_2 complex, we warm the surface to 120 K and cool it back to 4.5 K. The temperature cycling does not change the K−O_2 complex distribution. Overall statistics of K-O_2 dot and island numbers based on several thousand elements are also made. The number density ratios between K-O_2 dots and triangles are nearly same before and after temperature cycling (see Figure S3f), indicating that the K−O_2 complexes are stable with respect to the O_2 molecule desorption or dissociation up to 120 K.

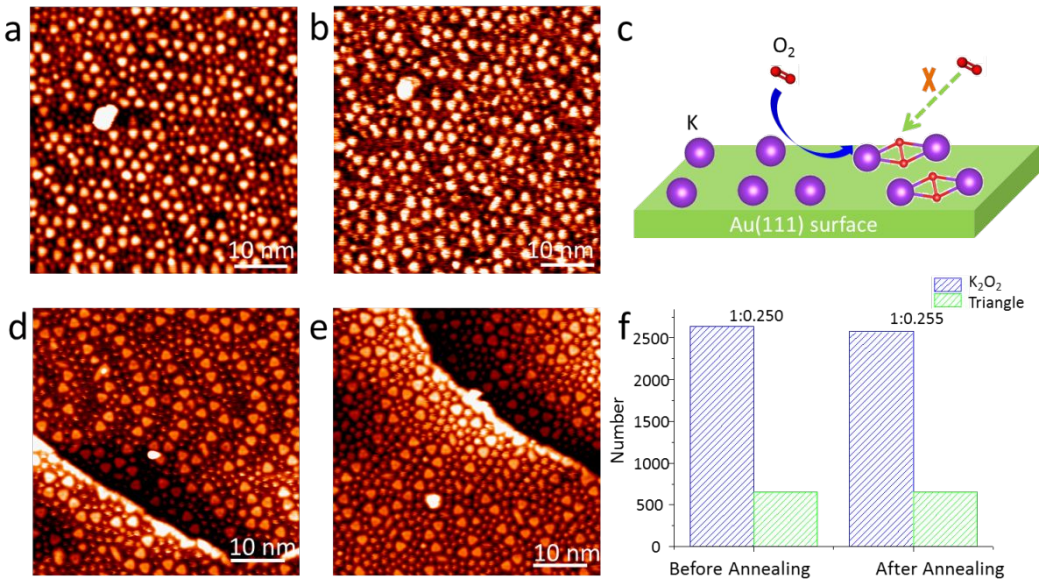


Figure S3. (a) Before O_2 dosing, and (b) After O_2 dosing. After the initial O_2 dose, there is no further O_2 adsorption and K−O_2 complexes remain unchanged. (c) Schematic diagram of O_2 capture by bare K atoms to form K_2O_2 dots. After all of K atoms are captured by K−O_2 complexes, no further O_2 adsorption occurs. (d)-(f) Statistical distribution of K−O_2 dots and triangle islands after cycling to different temperatures. (d) Initial image before the cycling process where O_2 is adsorbed at 4.5 K. (e) STM image of K−O_2 complexes after cycling the sample to ~120 K and back to 4.5 K to record the image; (f) the ratios of K−O_2 dots to triangle islands before and after temperature cycling process are 0.250 and 0.255, i.e., they are unchanged within the counting statistics of measurements.

IV. Charge redistribution analysis

To understand more details of the nature of O_2 in the K_2O_2 on Au(111) surface. The charge redistribution on O_2 before and after forming K_2O_2 on Au(111) surface is shown in Figure S4. It is calculated as $\rho(O_2) + \rho(Au+K_2) - \rho(Au+K_2O_2)$. It can be seen that the dominant electron transfer is from the Au surface (where the two K atoms have already transferred their electrons to Au) to the O_2 π^* orbital. In addition, there is also charge transfer from the σ to the O_2 π^* orbital of O_2, which lengthens the O−O bond and affects its stretching frequency

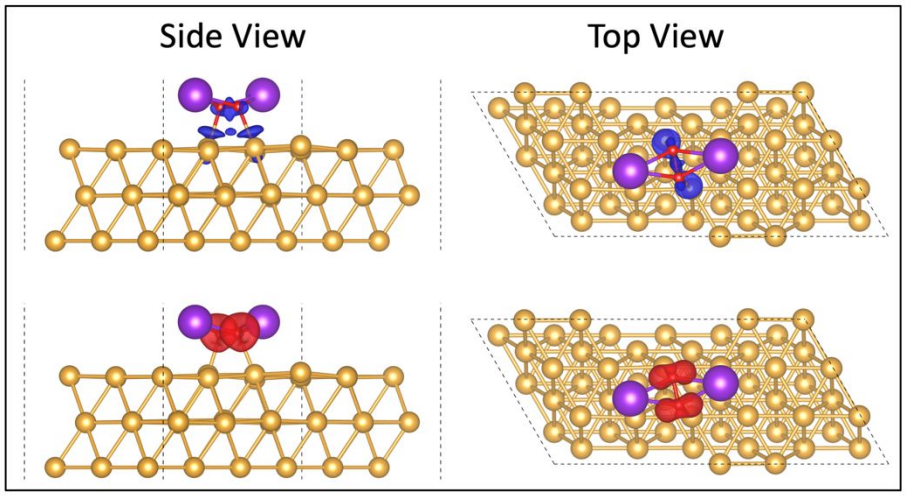


Figure S4. Side and top views of charge redistribution on O_2 before (top) and after forming K_2O_2 on Au(111) surface (bottom). The blue area is electron density loss, while the red is electron density gain.