

## Supporting Information:

### **Direct Visualization of a Gold Nanoparticle Electron Trapping Effect**

Oscar Bentley Jerdmyr Williams<sup>a‡</sup>, Khabiboulakh Katsiev<sup>b‡</sup>, Byeongjin. Baek<sup>c</sup>, George Harrison<sup>d</sup>, Geoff Thornton<sup>\*a</sup>, Hicham Idriss<sup>\*a,b,#</sup>.

‡ Equal contribution

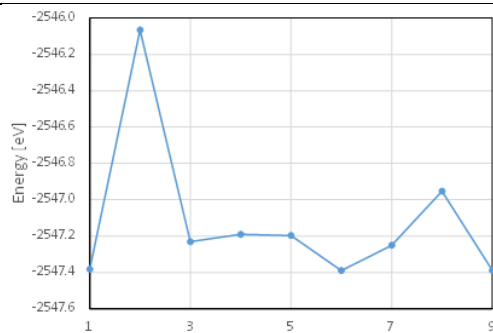
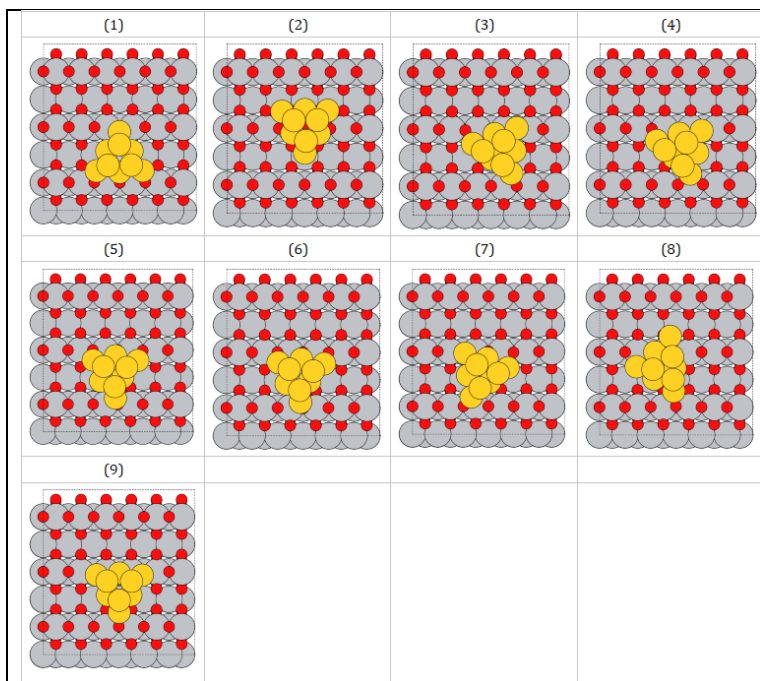
<sup>a</sup>Department of Chemistry and London Centre for Nanotechnology (LCN), University College London (UCL), WC1H 0AH, London, UK

<sup>b</sup>Surface Science and Advanced Characterisation, SABIC-CRD at King Abdullah University for Science and Technology (KAUST), Thuwal, 23955, Saudi Arabia

<sup>c</sup>SABIC Global Corporate Research, Sugar Land, Texas 77478, United States

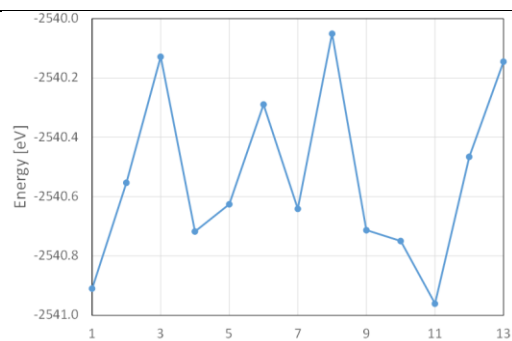
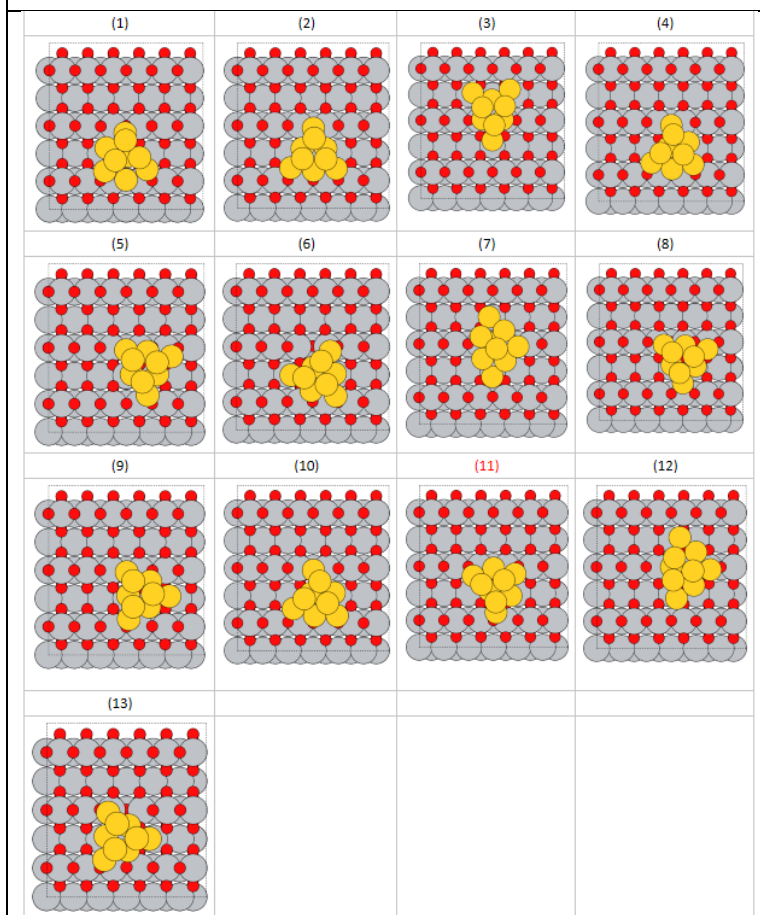
<sup>d</sup>KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), King Abdullah University for Science and Technology (KAUST), Thuwal, 23955, Saudi Arabia

<sup>#</sup>Present address: Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany



Au<sub>9</sub>/TiO<sub>2</sub>(110) stoichiometric.

Total energies of all configuration. The configuration (6) is the most stable and was chosen for the study.



Au<sub>9</sub>/TiO<sub>2</sub>(110) reduced

Total energies of all configuration. The configuration (11) is the most stable and was chosen for the study.

**Figure S1.**

All studied gold (Au<sub>9</sub>) clusters configurations deposited on stoichiometric TiO<sub>2</sub> (110) (top) and reduced TiO<sub>2</sub> (110) (bottom).

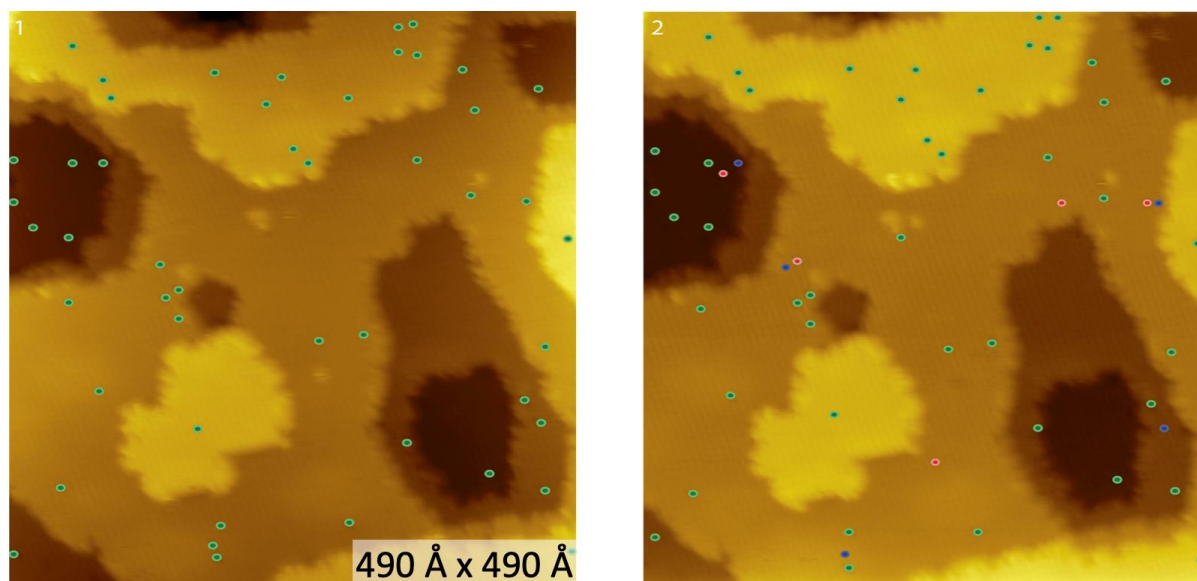
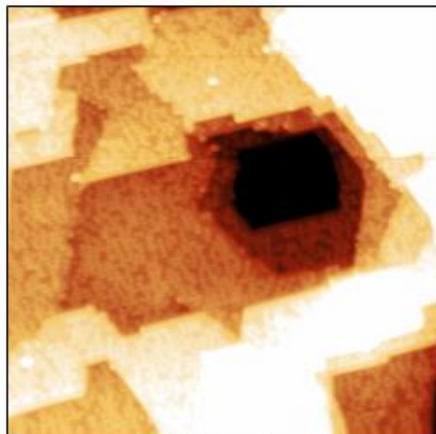


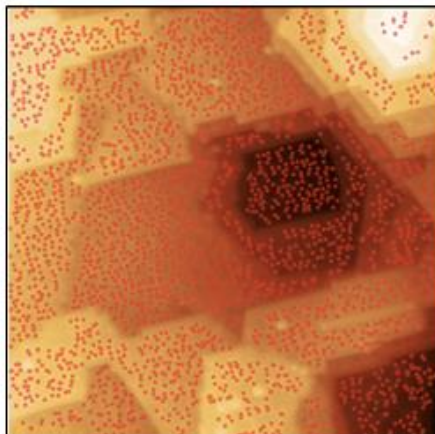
Figure S2.

Images of  $2 \times 1$  benzoates over  $\text{TiO}_2(110)$  surface. The second image was taken 120 s after the first one. Green are empty sites that remained constant, red are new empty sites formed, and blue are sites that were previously empty but are now occupied. Often blue and red points occur in pairs, suggesting diffusion. Most empty sites were unchanged; 92 % “immobile”. Images  $490 \text{ \AA} \times 490 \text{ \AA}$  taken at 2.02 V, 0.03 nA.

Clean Rutile  $\text{TiO}_2(110)$  - 1x1  
Images 52 x 52  $\text{nm}^2$



As imaged, -OH (br) are the bright features on the terraces.



Red dots label the -OH (br) species of a large area of the image on the left

Number of -OH (br) = 1860  
Exact Size = 2756  $\text{nm}^2$   
 $\text{Ti}_{5c} = 14203$

Density of -OH (br) = 0.67/ $\text{nm}^2$   
Coverage of -OH (br) with respect to  $\text{Ti}_{5c} = 0.13$  ML

### Figure S3

Examples for the counting the number of -OH species of a clean surface. The degree of hydroxylation at 300K of the surface did not affect the order or coverage of benzoate species.

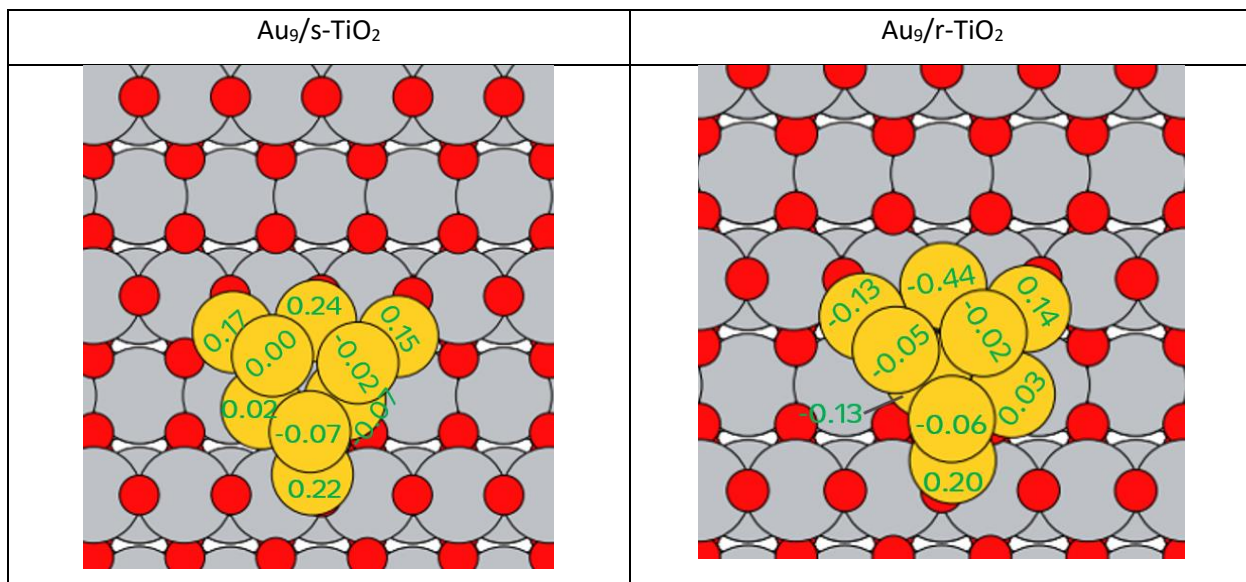


Figure S4.

Local Bader charge distribution of the Au<sub>9</sub> cluster deposited on the s- and r-TiO<sub>2</sub>(110) surfaces.

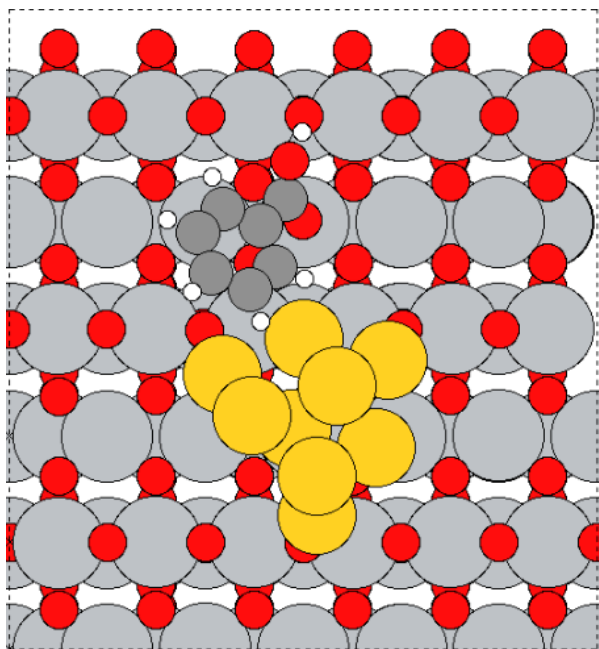
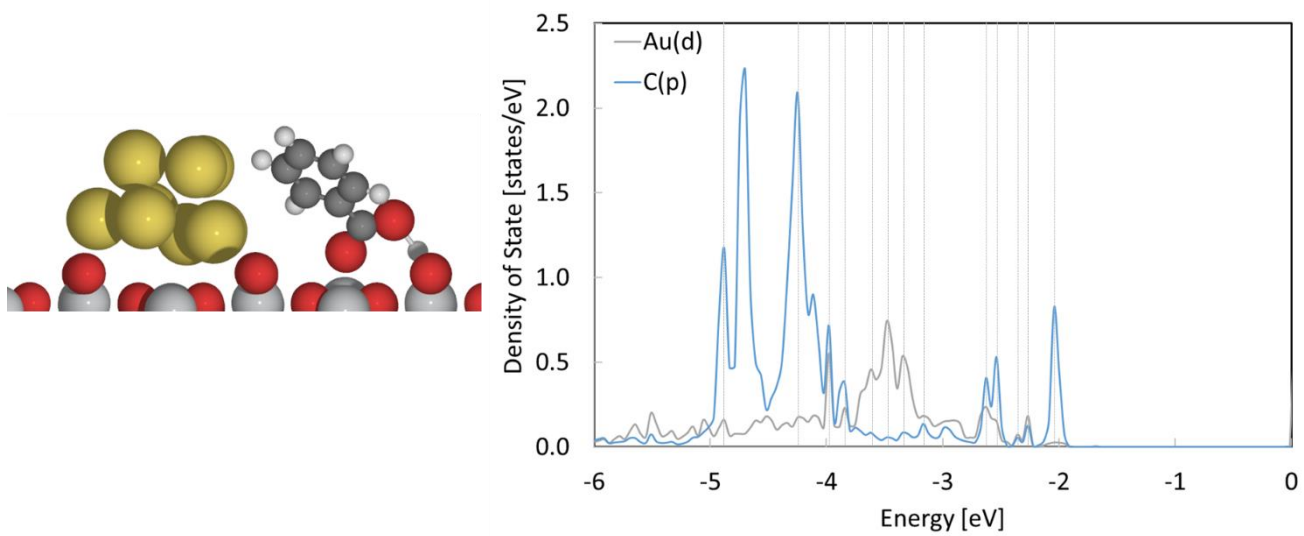


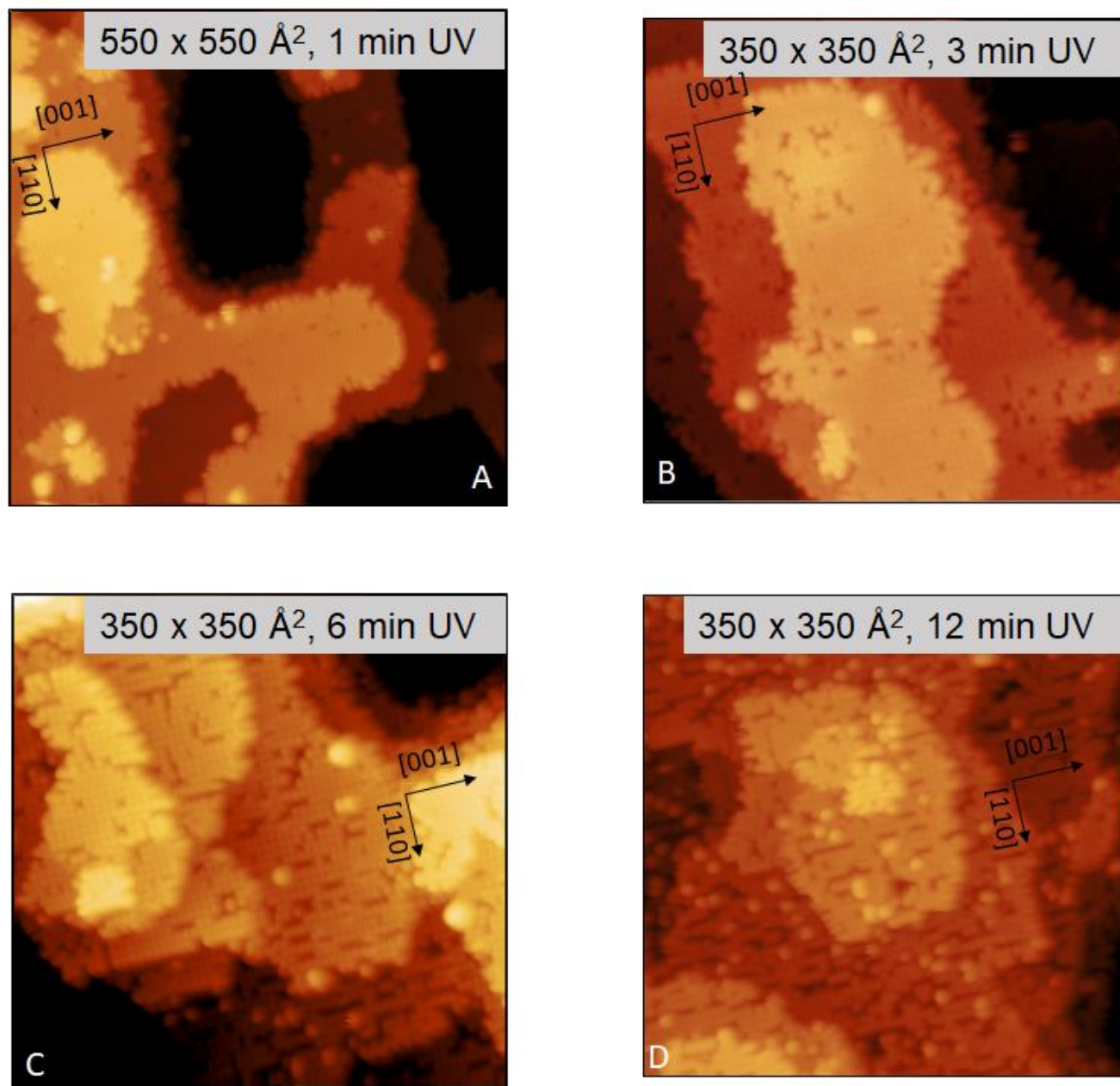
Figure S5.

Benzoic acid adsorption on Au<sub>9</sub>/r-TiO<sub>2</sub> (110).



**Figure S6.**

Benzoic acid adsorption on Au<sub>9</sub>/s-TiO<sub>2</sub> (110) and pDOS as extracted from DFT+U for Au(5d) and C(2p) states.



**Figure S7**

Effect of UV-Vis irradiation of benzoate-Au/TiO<sub>2</sub> (110) single crystal at 300K (light is delivered using a Xenon Arc 300-W MAX-303 Asahi Spectra Xe lamp; flux = 690 mWcm<sup>-2</sup> over a range of wavelengths from 320 - 630 nm). Benzoate (C<sub>6</sub>H<sub>5</sub>COO(a)) coverage is 0.41 ML and Au cluster coverage is about 0.1 MLE. Note the increasing relative preferential formation of empty sites (due to reaction) along the [001] direction when compared to the [110] direction. Image D is more complex due to the formation of “possible” reaction products that did not desorb (this can be benzene or even biphenyl) and therefore accumulate with time.