

Investigating the effect of UV light pre-treatment on the oxygen activation capacity of Au/TiO₂

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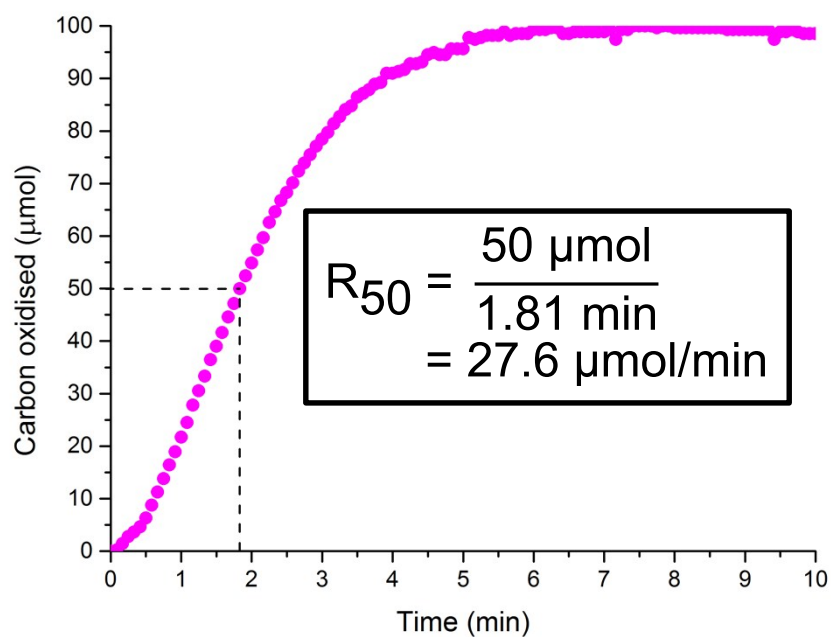


Figure S1. A typical reaction curve of 1 at% Au/TiO₂ showing the calculation of R₅₀ for the oxidation of 100 μmol formic acid after 30 min UV light pre-illumination. The 50 % formic acid oxidised point is determined to be at 50 μmol carbon oxidised.

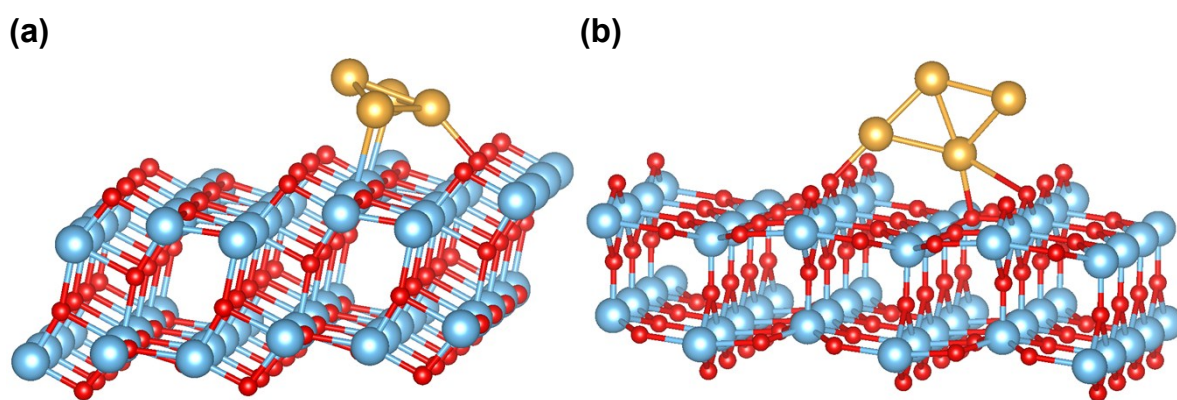


Figure S2. TiO₂ slab models used for DFT calculations for: (a) Au on anatase (101); (b) Au on rutile (110).

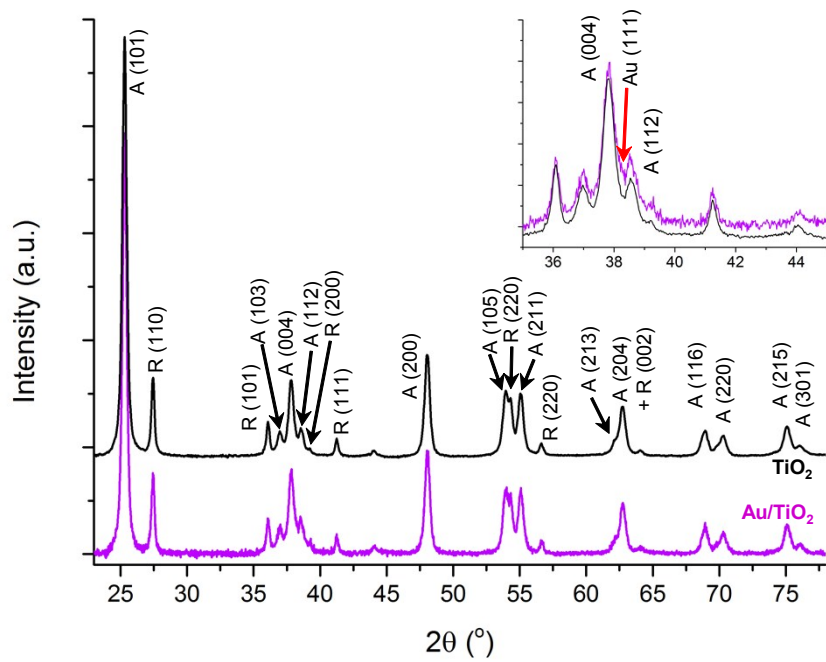


Figure S3. XRD profiles of neat TiO_2 and as-prepared Au/TiO_2 showing the presence of crystalline Au nanoparticles^{1,2}. Au crystal size could not be determined due to interference from the anatase and rutile peaks.

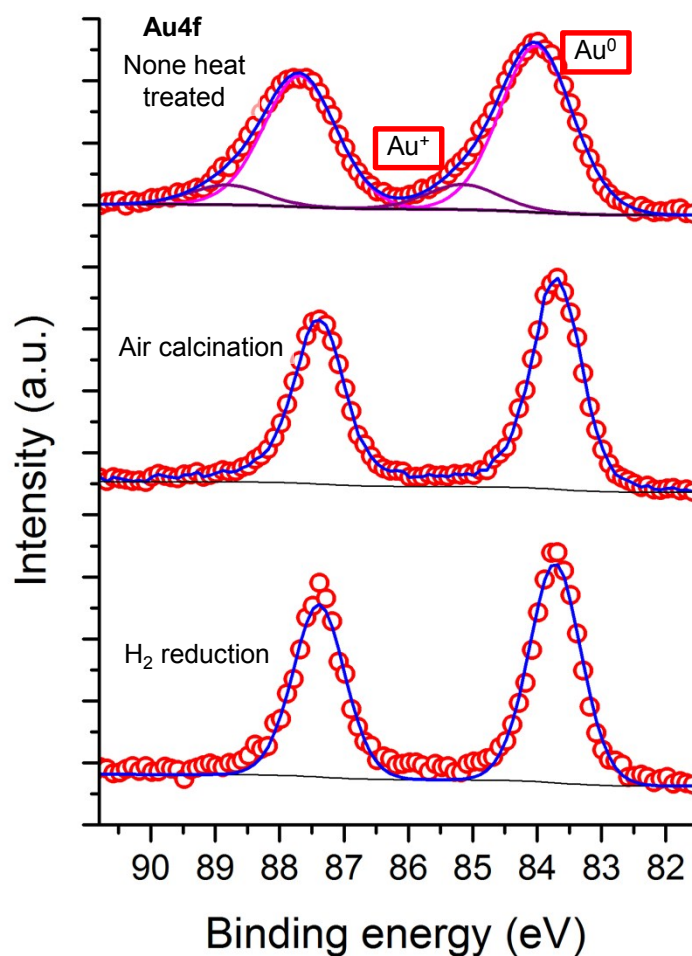


Figure S4. XPS Au4f core levels for 1.0 at% Au/TiO₂ before any heat treatment, after air calcination at 250 °C, and after H₂ reduction at 450 °C (as-prepared sample).

The XPS Au4f core level spectra show the change in Au oxidation states during the synthesis process. The Au oxidation state after the deposition-precipitation step has a higher oxidation state, as indicated by the presence of Au⁺ species. The Au⁺ species quickly disappear after air calcination, producing metallic Au⁰ deposits on the TiO₂ support. The H₂ reduction step at high temperature is necessary to achieve highly metallic state and to improve the Au-TiO₂ interaction.

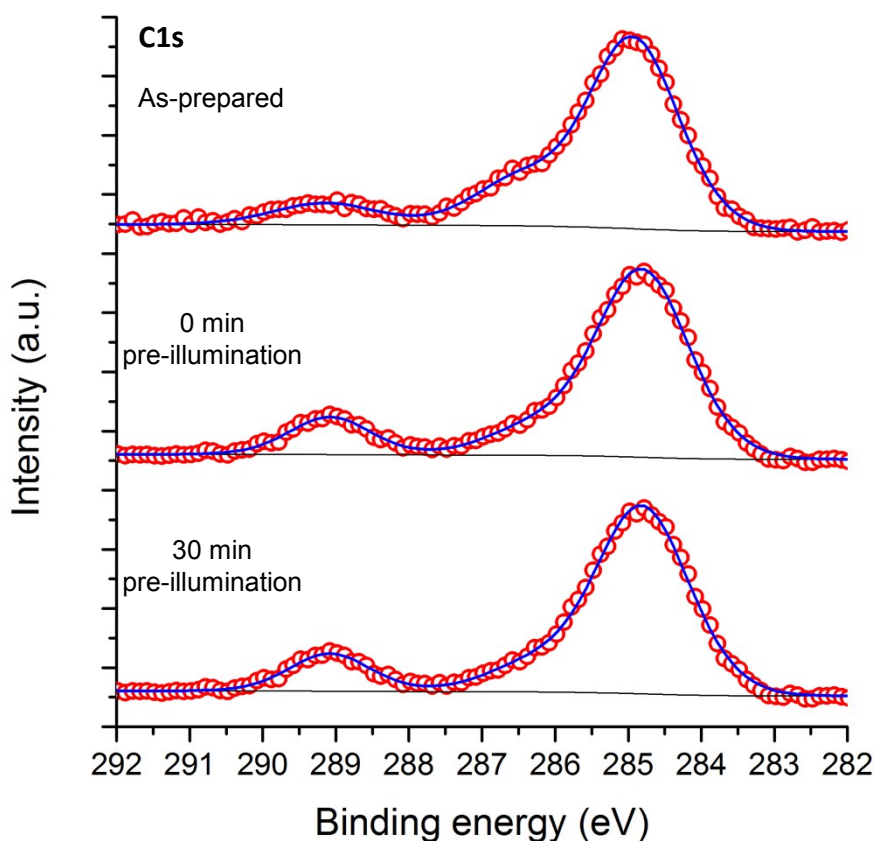


Figure S5. XPS C1s core levels for 1.0 at% Au/TiO₂ as-prepared, at 0 min light pre-illumination (i.e. immersed in water), and following 30 min light pre-illumination. Total carbon species on the Au/TiO₂ surface were 12.1 at%, 11.1 at%, and 11.2 at%, respectively, and are attributed to adventitious carbon.

Based on the XPS C1s core level spectra, UV light pre-illumination did not achieve significant photocleaning effect (i.e. no reduction in the amount of surface carbon species) on Au/TiO₂ prepared by deposition-precipitation, contrary to our observation on the Pt/TiO₂ prepared by photodeposition in the presence of organic hole scavenger³. It is therefore believed that the surface of Au/TiO₂ prepared by deposition-precipitation in the absence of organic additives is reasonably clean in its as-prepared state, and photocleaning of the surface during UV light pre-illumination has minimal contribution towards the enhancement of formic acid oxidation rate.

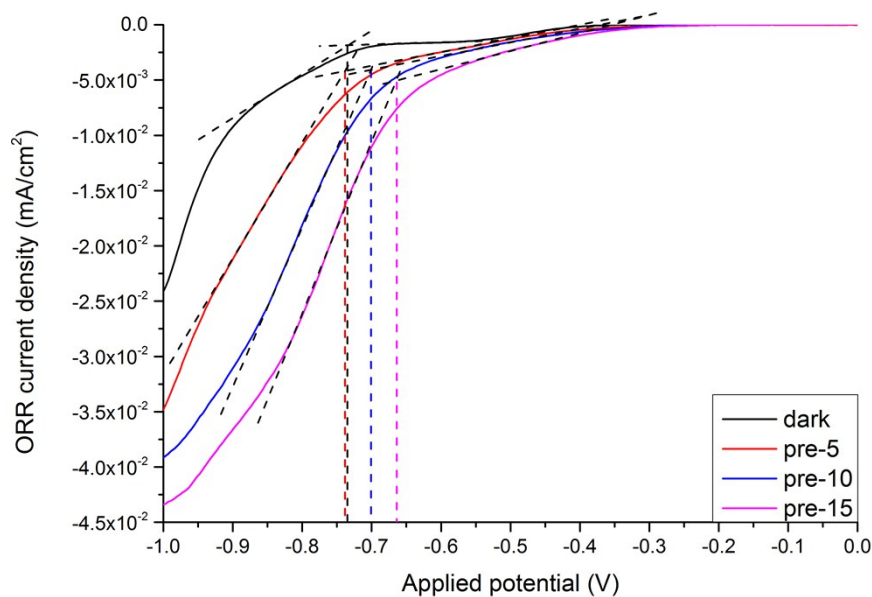


Figure S6. Current (I) – voltage (V) curve of Au/TiO₂ in the dark (black), after 5 min (red), 10 min (blue), and 15 min (pink) pre-illumination.

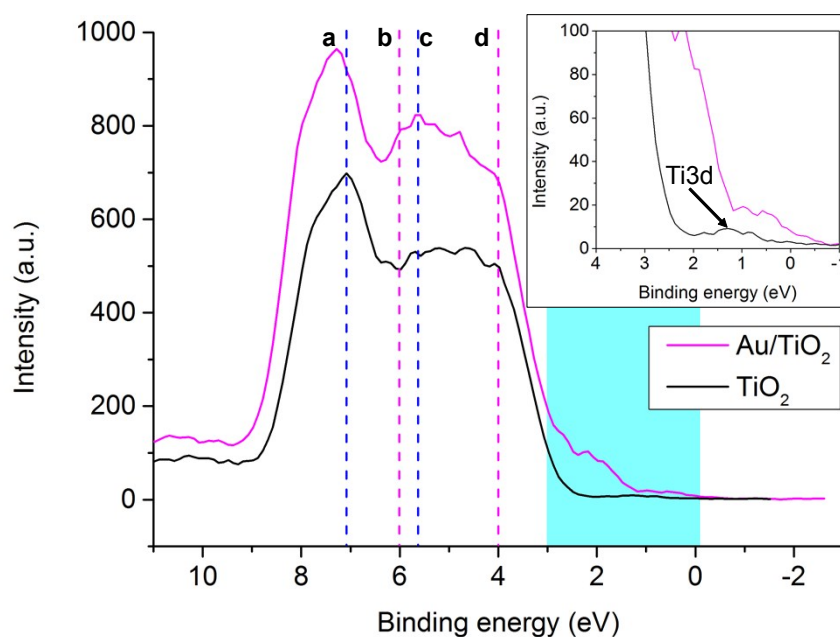


Figure S7. XPS valence band spectra of TiO₂ and Au/TiO₂. New valence states from the presence of Au nanoparticles are highlighted in light blue. Inset: valence band of TiO₂ and Au/TiO₂ at low binding energies, showing signal of Ti3d in TiO₂ diminishing after Au deposition, suggesting electron transfer from Ti surface defect sites to Au and strong Au-Ti interaction. NB: O2p bonding state (a) and non-bonding state (c); Au5d_{3/2} (b) and Au5d_{5/2} (d).

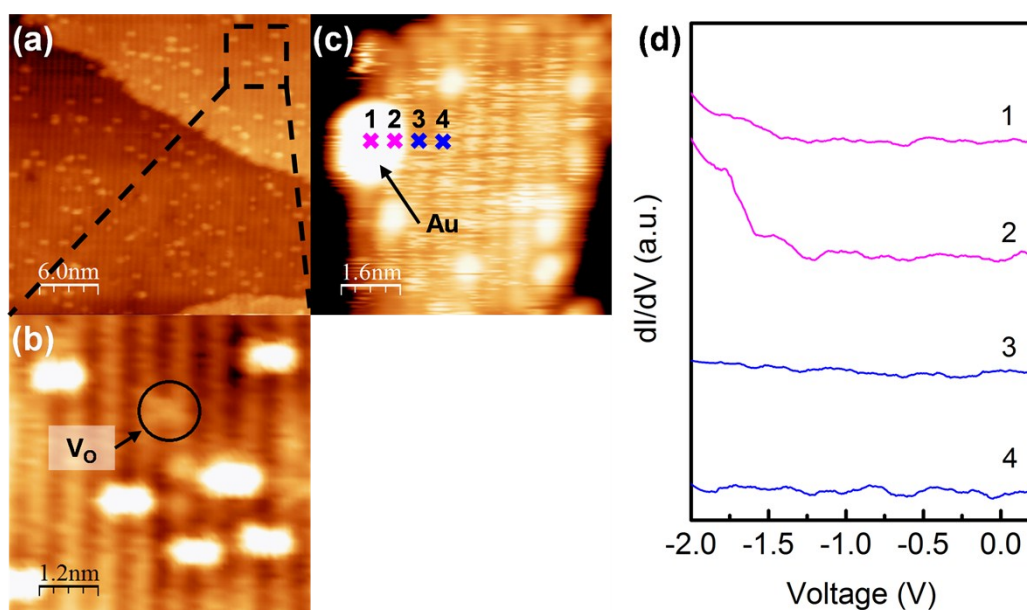


Figure S8. STM images showing: (a) the surface morphology of Au/TiO₂; (b) a selected area revealing an oxygen vacancy (V_O); (c) the presence of an Au nanocluster on TiO₂; (d) STS across the Au/TiO₂ interface showing the new valence states intensity gradient on the Au nanoparticle ($V_{\text{sample}} = 1.5 \text{ V}$, $I = 100 \text{ pA}$, lock-in modulation $V = 20 \text{ mV}$ at 937 Hz).

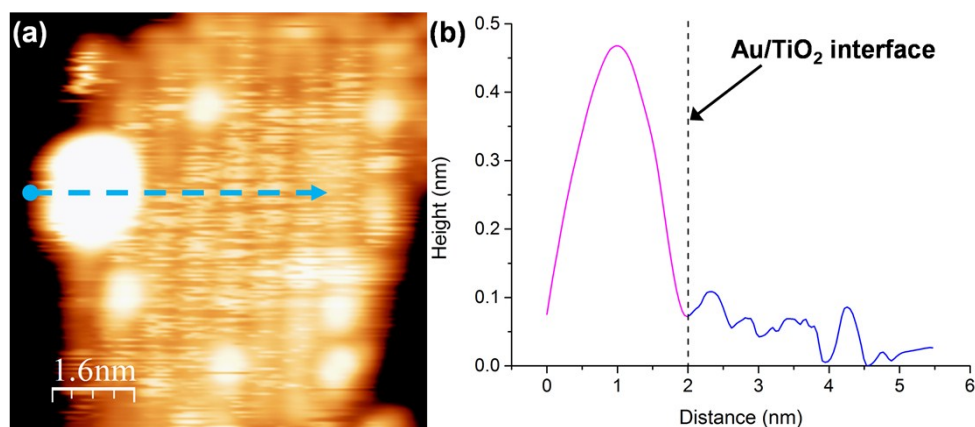


Figure S9. (a) STM image of Au nanocluster on TiO₂; (b) Line profile of Au/TiO₂ as indicated by the blue dotted line in (a). The purple line segment and the blue line segment represent the Au nanocluster region and TiO₂ region, respectively, with the black dotted line highlighting the Au/TiO₂ interface.

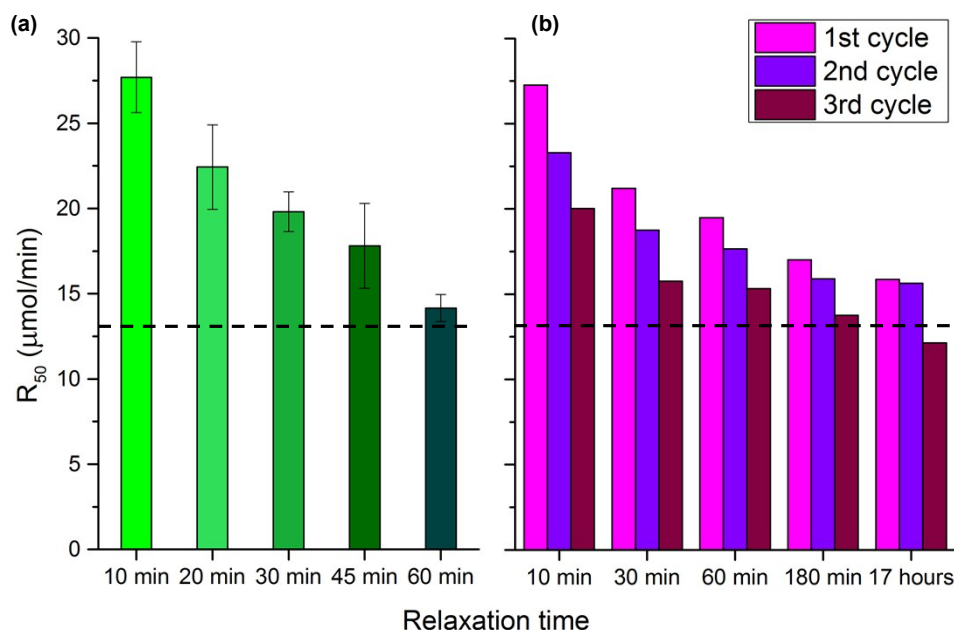


Figure S10. Stability of catalytic performance of Au/TiO₂: (a) R₅₀ of 1 at% Au/TiO₂ after 30 min of UV pre-illumination. A total of 500 μmol of formic acid was injected into the system over five sequential 100 μmol injections. Each injection was performed immediately after all the formic acid in the system from the previous injection had been oxidized. No UV light pre-treatment was conducted between injections. (b) R₅₀ of 1 at% Au/TiO₂ at various relaxation times. A total of 500 μmol of formic acid was injected into the system in the form of five sequential 100 μmol injections at various time points over 17 hours with the five injections regarded as one cycle. After all the formic acid from the fifth injection had been oxidized, the Au/TiO₂ was re-illuminated for 30 min with UV light. The 17-hour experiment was repeated for three cycles. The horizontal black dotted lines in both graphs represent the R₅₀ of Au/TiO₂ without UV light pre-treatment.

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