Synthesis of Reactive Oxygen Species on Rutile TiO_2(110) Surface by atomic force microscopy: Superoxide and Ozone Molecules

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Electron-hole activation, transforming closed- to open-shell reactive oxygen species on photocatalytic TiO_2 surfaces, is essential for design of effective photocatalysts [1]. However, at atomic level, the activation mechanism of the oxygen species remains murky. To shed light, we used a combination of low-temperature AFM, KPFS under UHV conditions with density functional theory simulations to understand the atomic-scale mechanism of electron and hole injection into the chemisorbed oxygen species supported on the rutile TiO_2 (110) surface [2]. We demonstrate manipulation of closed-shell peroxo (O_2^{2-}) molecule by applied local electric field to induce its hopping between different adsorption sites or molecular rotation. We synthesized the open-shell superoxo (O_2^-) molecule by injecting a hole into the corresponding closed-shell form, Fig. 1. Combining applied local electric field with hole injection we have been able to activate a *tip-induced Langmuir-Hinshelwood reaction* leading to ozone (O_3) molecule formation and, for the first time, visualize its synthesis at atomic resolution, Fig. 1. We show that both species synthesized via hole injection are long-lived, directly demonstrating their prominent role in photocatalysis.

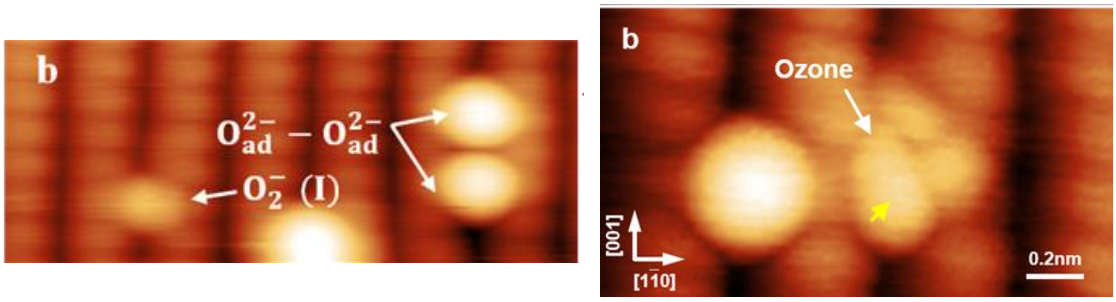

Figure 1. Reactive oxygen species synthesized on TiO_2 (110) surface by hole injection. Left panel: superoxide, O_2^-, Right panel: ozone, O_3^{2-}.

References

[1] H.H. Chen, C.E. Nanayakkara, V.H. Grassian, Chem. Rev. **112**, 5919 (2012).

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