Tip-activated single-atom catalysis: CO oxidation on Au adatom on oxidized rutile TiO_2 surface

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Abstract

Single-atom catalysis of carbon monoxide oxidation on metal-oxide surfaces is crucial for greenhouse recycling, automotive catalysis, but reports of the atomic-scale mechanism are still scarce. In this study, we show that charging single gold (Au_1) atoms on oxidized rutile titanium dioxide (TiO_2) surface, both positively and negatively, considerably promotes adsorption of carbon monoxide (CO) using atomic force microscopy (AFM)/Kelvin probe force microscopy (KPFM). Two different carbon monoxide adsorption geometries on gold atoms are identified. We demonstrate full control over the redox state of adsorbed gold single (Au_1) atoms, CO adsorption geometry, and CO adsorption/desorption by the atomic force microscopy tip. On charged Au_1 atom, we activate Eley-Rideal oxidation reaction between CO and a neighboring oxygen adatom by the tip. Our results provide unprecedented insights into CO adsorption and suggest that the Au dual activity for CO oxidation after electron or hole attachment is also the key ingredient in photocatalysis under realistic conditions.

Background & Results

The study of the outstanding catalytic properties of single-atom catalysts on metal oxide surfaces is becoming a new frontier in heterogeneous catalysis. Homogeneous single-atom catalysts achieve high activity and selectivity through large coverage and high aspect ratios, and offer great potential for fundamental understanding of atomic-scale catalytic reactions. Single gold atoms may play a role in a variety of catalytic reactions that is unprecedented for conventional Au-based catalysts. However, the physical origin of single-atom catalysts on the atomic scale is still the subject of intense debate. In particular, the catalytic performance of Au nanoparticles may differ from that of single-atom gold catalysts. An important missing link is the ability to directly probe and understand the local environment and charge state of the active site with atomic resolution.

The following results were obtained. 1) Using AFM/KPFM, CO adsorption was significantly enhanced when both positive and negative charges were applied to Au_1 on the rutile oxide TiO_2 surface (Fig. 1). 2) Regarding CO adsorption, two different forms of CO adsorption on Au_1 were identified (Fig. 2). The redox state of adsorbed Au_1, the CO adsorption geometry, and CO adsorption/desorption by the AFM tip were fully controlled. 3) Eley-Rideal oxidation reactions between CO and adjacent oxygen atoms on charged Au_1 (Au_1^- and Au_1^+) were found to be activated by the AFM tip. 4) The manipulated charge state of the noble metal atoms is the key to the adsorption of carbon monoxide, which can be catalyzed by the application of an electric field (Fig. 3).

Significance of the research and Future perspective

Because the oxidation reaction by noble metal atoms on metal oxide surfaces can be observed with atomic resolution, this technology will greatly enhance the design and evaluation of new nanocatalytic materials. Therefore, this technology is expected to become a new fundamental technology for realizing innovative photocatalytic and solar cell materials in the future.

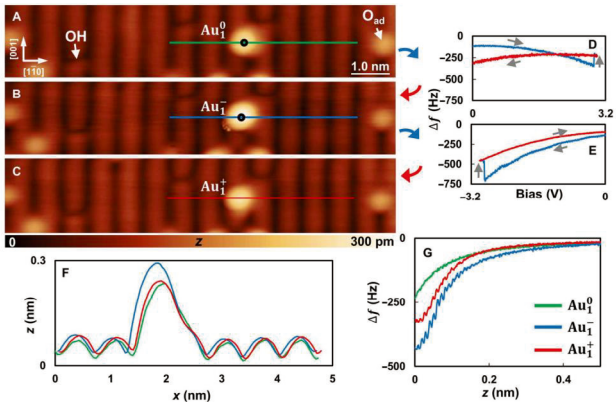

Fig. 1. Charge manipulation of a single Au atom on oxidized rutile TiO_2 (110) surface. (A to C) AFM images of Au_1^0, Au_1^- and Au_1^+. (D-E) Bias voltage dependence of frequency shift. Tip position is indicated by a black circle in (A) and (B). (F) Constant Δf line profiles measured on top of the voltage dependence of frequency shift as indicated by the same colors in (A) to (C) and (G). (G) $\Delta f(z)$ spectra measured over the Au_1^0, Au_1^- and Au_1^+.

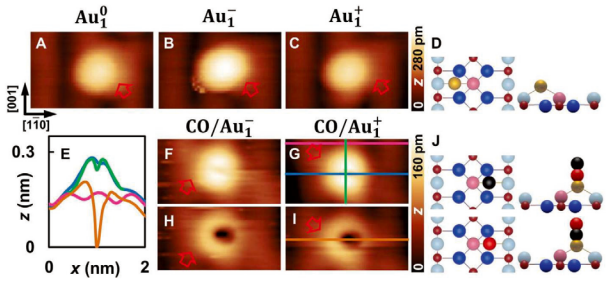

Fig. 2. Atomic-scale CO adsorption on the Au_1/O-rutile TiO_2 (110) surface. (A-C) AFM images of Au_1^0, Au_1^- and Au_1^+. (F-I) AFM images of CO adsorbed Au_1^- and Au_1^+ (F-G: bean shape, H and I: donut shape). (D and J) Schematic models of TiO_2 (110) surface with Au_1 adsorbed and CO adsorbed on Au_1, respectively. (E) Bean shape (green and blue lines) and donut shape (orange line) of CO Adsorbed Au_1^+ height.

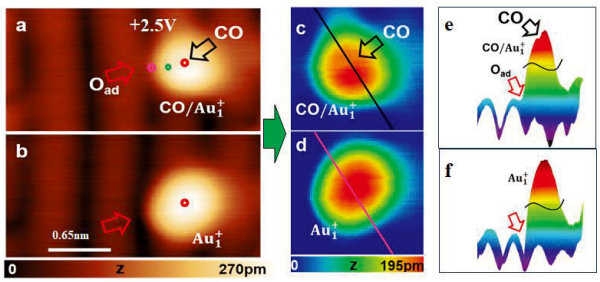

Fig. 3. Single-atom catalysis based on Eley-Rideal mechanism. (a) AFM image of CO/Au_1^+ on oxidized rutile TiO_2 (110) surface before and (b) after an electric field was applied. (c) Contrast-enhanced image of CO/Au_1^+ before and (d) of Au_1^+ after the reaction. (e-f) Corresponding line profiles in (c) and (d) with different color.

Patent	
Treatise	Adachi, Yuuki; Štich, Ivan; Li, Yanjun et al. Tip-activated single-atom catalysis: CO oxidation on Au adatom on oxidized rutile TiO_2 surface. Science Advances. 2023, 9(39), eadi4799. doi:10.1126/sciadv.adi4799 Adachi, Yuuki; Štichs, Ivan, Li, Yanjun et al. Mechanocatalysis of CO to CO_2 on TiO_2 surface controlled at atomic scale. Nano Research. 2024, 17, 5826–5834. doi:10.1007/s12274-024-6539-z Adachi, Yuuki; Sugawara, Yasuhiro; Li, Yanjun. Probing CO on a rutile TiO_2(110) surface using atomic force microscopy and Kelvin probe force microscopy. Nano research. 2022, 15(3), 1909-1915. doi: 10.1007/s12274-021-3809-x
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