

Catalytic Mediation by Ti-deficient $Ti_{1-x}O_2$ Pillars at a Gold Nanoparticle- TiO_2 Boundary

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The remarkable catalytic activity of highly dispersed gold nanoparticles on TiO_2 for low-temperature CO oxidation has been of tremendous interest. The catalytic activity has been attributed to structural features, such as particle size¹⁻⁵, shape^{1-2, 4-6}, and support¹⁻⁶, particularly at the periphery and/or surface of the gold particles. The adsorption and activation of O_2 at Au/oxide catalysts via electronic origin of the contact^{3-4,6} has been proposed as a critical step in the CO oxidation pathway. Recent *in situ* experiments with O_2 exposure to gold-deposited $TiO_2(110)$ surfaces demonstrated the nucleation of TiO_2 islands on the $TiO_2(110)$ surface^{5,7}. Thus, O_2 is adsorbed at the TiO_2 surface, which can give rise to zero-order kinetics for CO oxidation¹. It remains unclear how the edges and/or periphery of the gold particles behave under O_2 exposure. The periphery has been proposed as the activation site for the CO oxidation pathway, since the catalytic activity, which shows a d^{-2} dependence¹, increases markedly for small particles with diameters below 2-3 nm^{1,5,8}. Here, we observed Au/ TiO_2 interfaces using *in situ* gas-injection transmission electron microscopy (TEM), and found $Ti_{1-x}O_2$ ($x > 0$) regions in TiO_2 pillars (See Figs 1-2) growing beneath the gold nanoparticles during O_2 exposure at 100 Pa. Pillars grew in O_2 and O_2+H_2O environments, but not in N_2 or H_2 . The $Ti_{1-x}O_2$ ($x > 0$) region had a different chemical composition from the TiO_2 substrate, with Ti^{3+} and $O^{(2-\delta)}$ ($\delta > 0$) in its electron energy loss spectra. The periphery of the $Ti_{1-x}O_2$ region at the Au/ TiO_2 contact is a candidate source of activated oxygen in the CO oxidation pathway.

References

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- [9] This work was supported by Grant-in-Aid for Scientific Research (A) of the Japan Society for the Promotion of Science (No. 16201020), and by CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Corporation (JST).

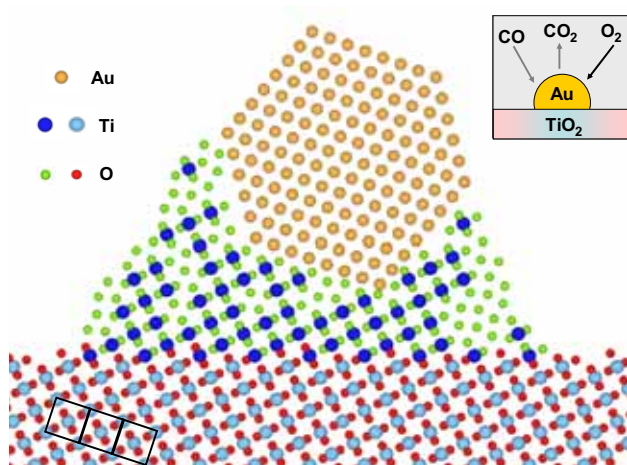


FIG. 1. Schematic view of a pillar, grown by O_2 exposure underneath a gold nanoparticle deposited on a TiO_2 substrate. Light blue and red dots represent Ti and O atoms, respectively, in the TiO_2 substrate. Blue and light green dots represent Ti and O atoms, respectively, in the pillar. The pillar has a different chemical composition from the TiO_2 substrate.

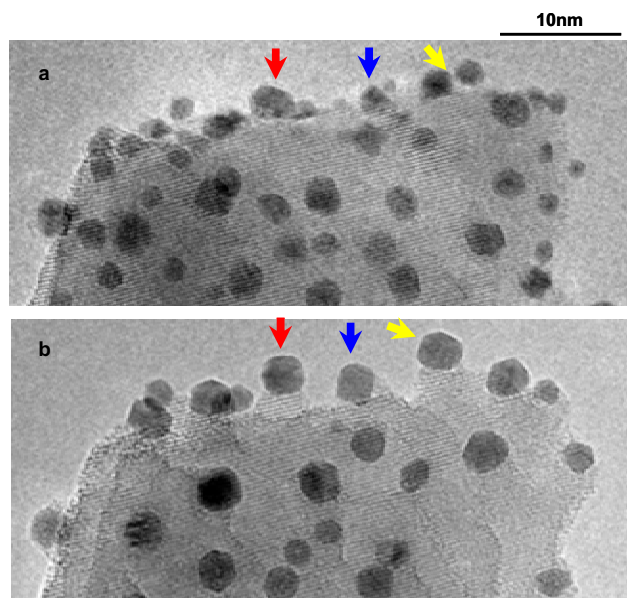


FIG. 2. *In-situ* TEM images (a) before and (b) after co-exposure of O_2 and H_2O at 100 Pa (O_2 : 95.6%, H_2O : 4.4%). Gold particles (dark contrast) in panel a have a distribution of diameters from 0.7–3.3 nm, centred at 2.2 nm. In panel b, the Au particles in panel a have been agglomerated, and the TiO_2 support protrudes at the positions of the Au deposits, as indicated by arrows. The agglomerated particles have a distribution of diameters from 1.3–4.2 nm, centred at 2.75 nm. The protrusions appeared after pillar growth during O_2 exposure. This morphology change was observed after exposure to O_2 or a mixture of O_2 and H_2O , but not after exposure to N_2 or H_2 . Most particles are multiply twinned particles (MTP).