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STEM imaging of Au nanoparticles on TiO_2 surface

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Gold (Au) nanoparticles dispersed on metal oxide supports are active catalysts for a variety of chemical reactions [1]. It has been well demonstrated that the unique catalytic activities strongly depend on the size of Au nanoparitcles and the properties of metal oxide supports [1,2], suggesting the importance of gold-support interface interactions at a nanometer regime. Extensive studies have been devoted to understand the origin of these activities, but the mechanism is still under debate because of the lack of structural information on the active gold on the support oxide surfaces. It is thus essential to characterize the atomic structures of nanosized Au on metal oxide surfaces, in order to truly understand the origin of the unique catalytic activities. In this study, we fabricated model Au nanoparticle/TiO_2 (110) interfaces by vacuum evaporation method. Atomic-resolution plan-view STEM imaging was carried out in order to directly observe the atomic structures of nanosized Au interacted with the TiO_2 (110) surface.

Atomic-resolution high-angle annular dark-field (HAADF) STEM images were taken with a 200-kV JEM-2100F TEM/STEM electron microscope (JEOL Ltd., Tokyo, Japan) equipped with an aberration corrector (CEOS GmbH, Heidelberg, Germany). The TiO_2 single crystal substrates (rutile structure) with (110) surface were prepared for TEM samples by a standard procedure using ion thinning method. The TEM samples were then annealed in air at 973 K for 0.5 hrs to remove surface damage layers and enhance the formation of atomically flat (110) surface. High-purity gold (99.95%) was deposited on the TEM sample surface by the vacuum evaporation method at room temperature.

FIG.1(a) shows a HAADF STEM image of rutile TiO_2 single crystal observed from the <110> direction. There are two types of bright spots with different image intensities as indicated by the arrows. These bright spots correspond to the two different Ti containing columns along the <110> projection. As schematically shown in the FIG.2 (b), the brighter spots correspond to the atomic columns with both Ti and O atoms (Ti-O column), while the darker spots correspond to the atomic columns with body-centred Ti atoms only (Ti-only column). The difference in the image contrasts mainly results from the difference in the atomic column occupancy of the two columns along the <110> axis. Signal from oxygen columns is too weak to be visible in the present HAADF imaging condition. FIG.2 (a)(b) shows plan-view HAADF STEM images of Au nanoparticles on TiO_2 (110) surface. It is clearly seen that the HAADF STEM detects the presence of Au islands on the TiO_2 surface by the strong Z-dependent image contrasts (Z: Au = 79, Ti = 22, O = 8). In the magnified image, the atomic structure of both Au nanoislands and TiO_2 support is simultaneously resolved. It is found that the projected sizes of Au islands are in the range of 1 ~ 5nm with the present deposition condition. In addition, we observed single Au atoms attached on the TiO_2 surface. The strong image intensity from the Au single atoms is only found at the on top positions of Ti-O columns in the [110]

projection. This result indicates that Au atoms are likely to attach specific sites on the TiO_2 surface. We also observed unique orientation relationships between Au nanoislands and TiO_2 support. These results indicate that there should be strong bonding interaction between Au atoms and TiO_2 (110) surface. This strong interfacial interaction may be related to the unique catalytic activities of nanosized Au on TiO_2 support.

References

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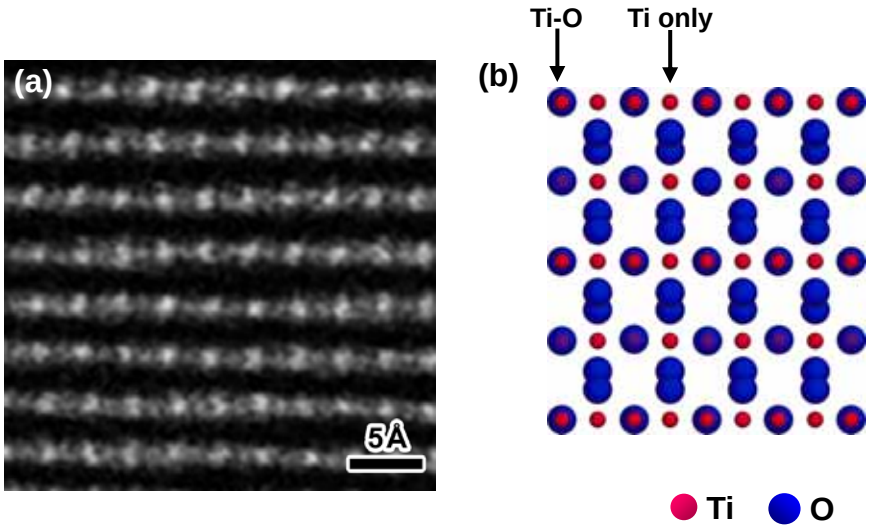

FIG. 1: (a) HAADF STEM image of rutile TiO_2 observed from <110> direction. (b) Corresponding TiO_2 crystal structure model.

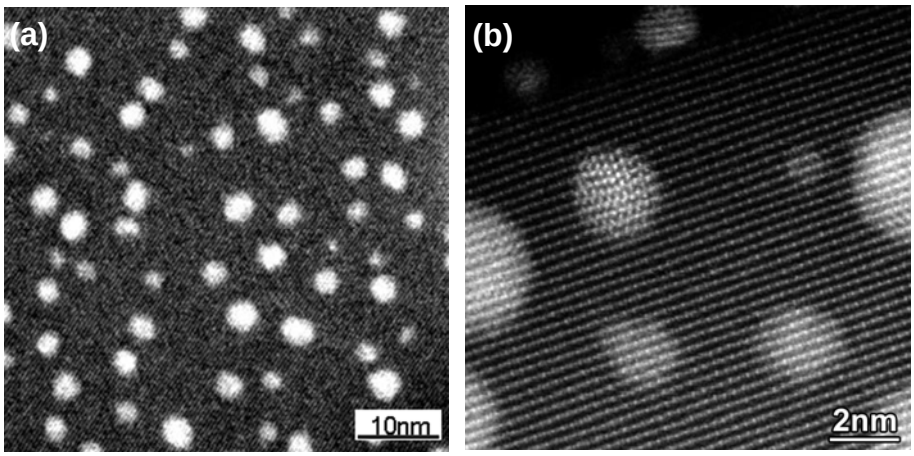

FIG 2:(a) Low and (b) high magnification HAADF STEM images of Au nanoparticles on TiO_2 (110).