Supporting Information

Crystal-plane-dependent Strong Metal-Support Interaction in Au/TiO_2

Lichen Liu,[a] Chengyan Ge,[a] Weixin Zou,[a] Xianrui Gu,[a] Fei Gao,[b]* Lin Dong [a,b]*

[a] Key Laboratory of Mesoscopic Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

[b] Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China

*** To whom correspondence should be addressed.**

Tel.: +86 25 83592290; fax: +86 25 83317761.

E-mail address: gaofei@nju.edu.cn (Fei Gao)
E-mail address: donglin@nju.edu.cn (Lin Dong)

Experiments

1. Synthesis of TiO_2 nanocrystals with different crystal planes exposed.

TiO_2 nanocrystals with different crystal planes exposed can be prepared according to our previous works.

References:

a) Liu, L.; Gu, X.; Ji, Z.; Zou, W.; Tang, C.; Gao, F.; Dong, L. Anion-assisted Synthesis of TiO_2 Nanocrystals with Tunable Crystal Forms and Crystal Facets and Their Photocatalytic Redox Activity in Organic Reactions. *J. Phys. Chem. C* **2013**, *117*, 18578-18587.

b) Liu, L.; Gu, X., Cao, Y.; Yao, X.; Zhang, L.; Tang, C.; Gao, F.; Dong, L. Crystal-Plane Effects on the Catalytic Properties of Au/TiO_2. *ACS Catal.* **2013**, *3*, 2768-2775.

2. Preparation of Au/TiO_2 catalysts with different TiO_2 crystal planes exposed.

Au nanoparticles are loaded on TiO_2 nanocrystals with different crystal planes exposed through deposition-precipitation. The loading amount of Au is 2%. 1g TiO_2 nanocrystal is put in a mixture of $HAuCl_4$ aqueous (0.0243 mol/L, 4.18 mL) and 0.605g urea. This mixture was kept stirring at 80 ^oC for 16 h. Then the suspension is certificated at 8000 r/min and wash with NaOH aqueous (0.1 mol/L). Afterwards, the product was washed with water for three times to neutral before it was dried at 60 oC. At last, the product was calcinated at 300 ^oC for 2 h in air.

Characterization

Transmission electron microscopy (TEM) images were taken on a JEM-2100 instrument at an acceleration voltage of 200 kV. The samples were crushed and dispersed in A.R. grade ethanol and the resulting suspensions were allowed to dry on carbon film supported on copper grids.

Ex situ X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 VersaProbe system, using monochromatic Al Kα radiation (1486.6 eV) operating at 25 W. The sample was outgassed overnight at room temperature in a UHV chamber ($<5\times10^{-7}$ Pa). All binding energies (BE) were referenced to the C 1s peak at 284.6 eV. The experimental errors were within ±0.1 eV. During the *ex situ* XPS experiments, the samples were first pre-treated with the corresponding atmosphere in an reaction chamber for 1 hour. Then the sample was sent to UHV chamber for XPS testing. After collecting XPS signals, the samples were sent to reaction chamber again for pre-treatment in another atmosphere.

In situ DRIFT spectra were collected from 400 to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1} (number of scans, 32) on a Nicolet 5700 FT-IR spectrometer equipped with a DTGS as the detector. The sample was pressed into a self-supporting wafer (about 15 mg) and mounted in a commercial controlled environment chamber (HTC-3). The wafer was pretreated with high purity N_2 at 200 ^oC for 1 h. After cooling to ambient temperature, the sample was pre-treated with H_2-Ar (10% H_2 by volume) or O_2-Au (10% O_2 by volume) at a rate of 5.0 mL min^{-1} for 1 hour. After cooling to ambient temperature, the sample was exposed to a controlled stream of CO-Ar (10% CO by volume) at a rate of 5.0 mL min^{-1} for 1 hour in order to be saturated. The spectroscopy was collected every minute.

Catalytic activity measurement

The CO oxidation activities of Au/TiO_2 catalysts were measured in a flow micro-reactor with a gas composition of 1.6 vol% CO, 1.6 vol % O_2 and 96.8 vol% N_2 at a space velocity of 300,000 mL g^{-1} h^{-1}, and 5 mg catalyst was used for each measurement in the kinetic study. The catalyst was pretreated in a N_2 stream at 200 ^{o}C for 1h to remove the adsorbed carbonates or H_2O. Then the catalyst was pre-treated with H_2 or O_2 for 1 hour under high temperature (250 ^{o}C, 300 ^{o}C or 350 ^{o}C). After pre-treatments, it was cooled to room temperature, after that, the mixed gases were switched on. Two columns and thermal conductivity detector (TCD) were used for the purpose of analyzing the production, column A with 13× molecular sieve for separating O_2, N_2 and CO, and column B, packed with Porapak Q for separating CO_2.

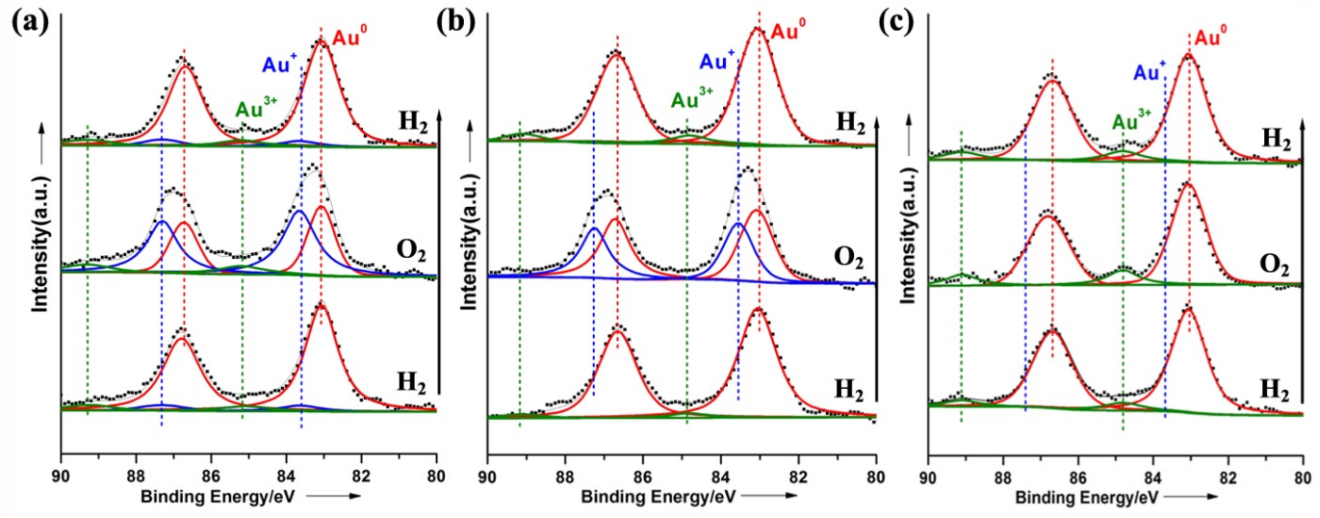

Fig. S1 Au 4f region of *ex-situ* XPS spectra of Au/Ti-100 (a), Au/Ti-101 (b) and Au/Ti-001 (c) pretreated under H_2 and O_2 at 250 °C.

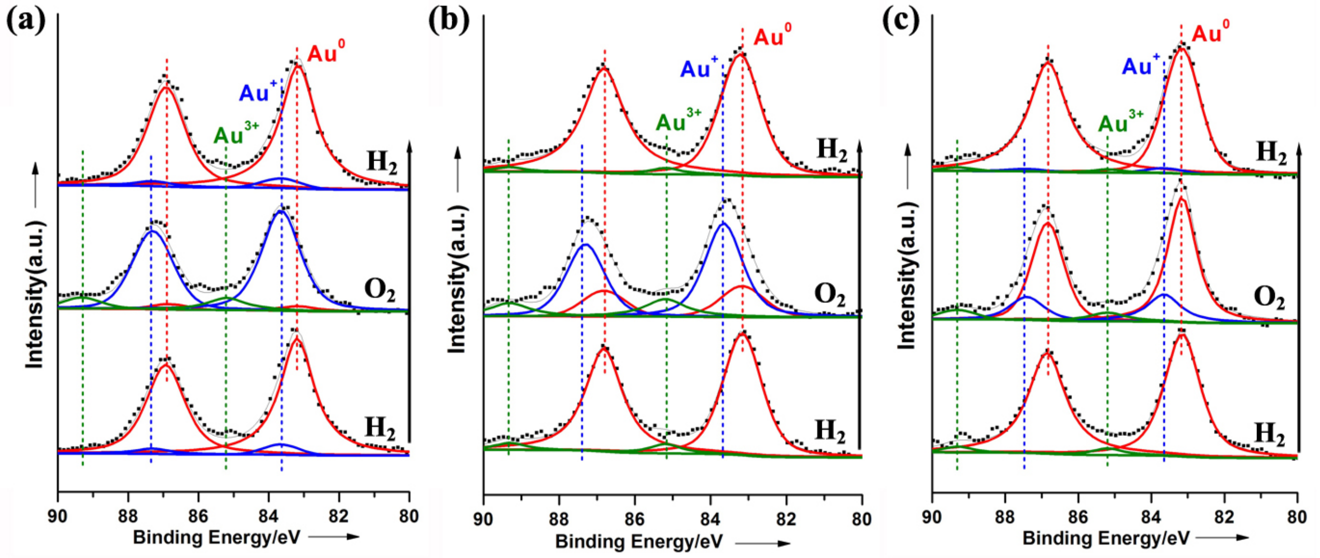

Fig. S2 Au 4f region of *ex-situ* XPS spectra of Au/Ti-100 (a), Au/Ti-101 (b) and Au/Ti-001 (c) pretreated under H_2 and O_2 at 300 °C.

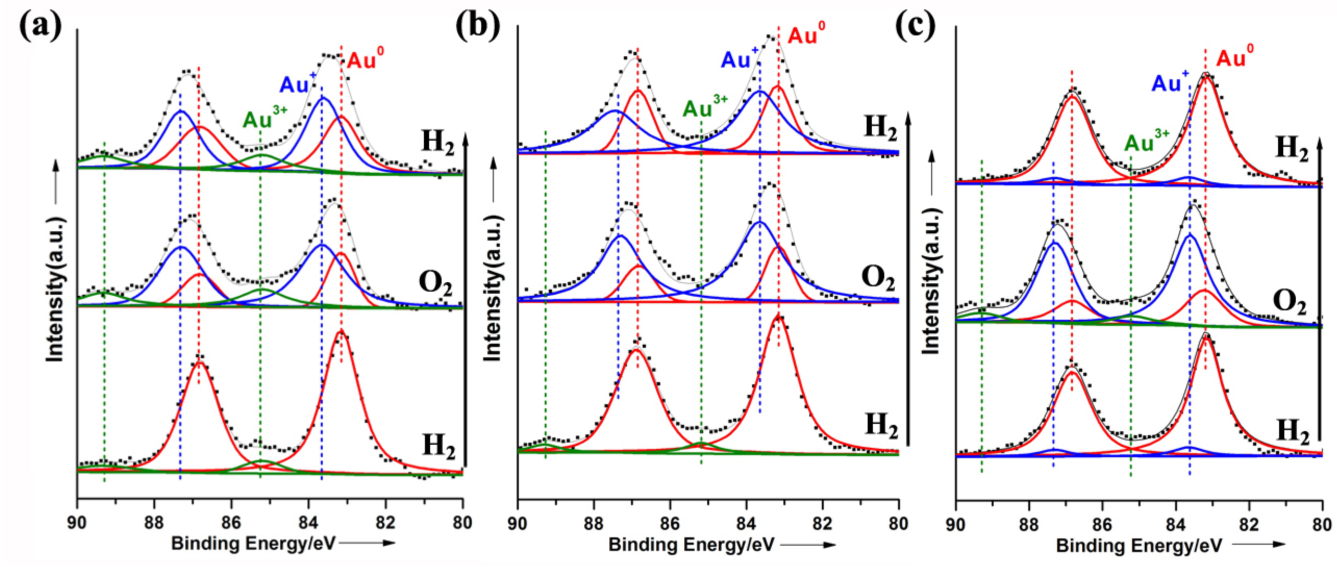

Fig. S3 Au 4f region of *ex-situ* XPS spectra of Au/Ti-100 (a), Au/Ti-101 (b) and Au/Ti-001 (c) pre-treated under H_2 and O_2 at 350 °C.

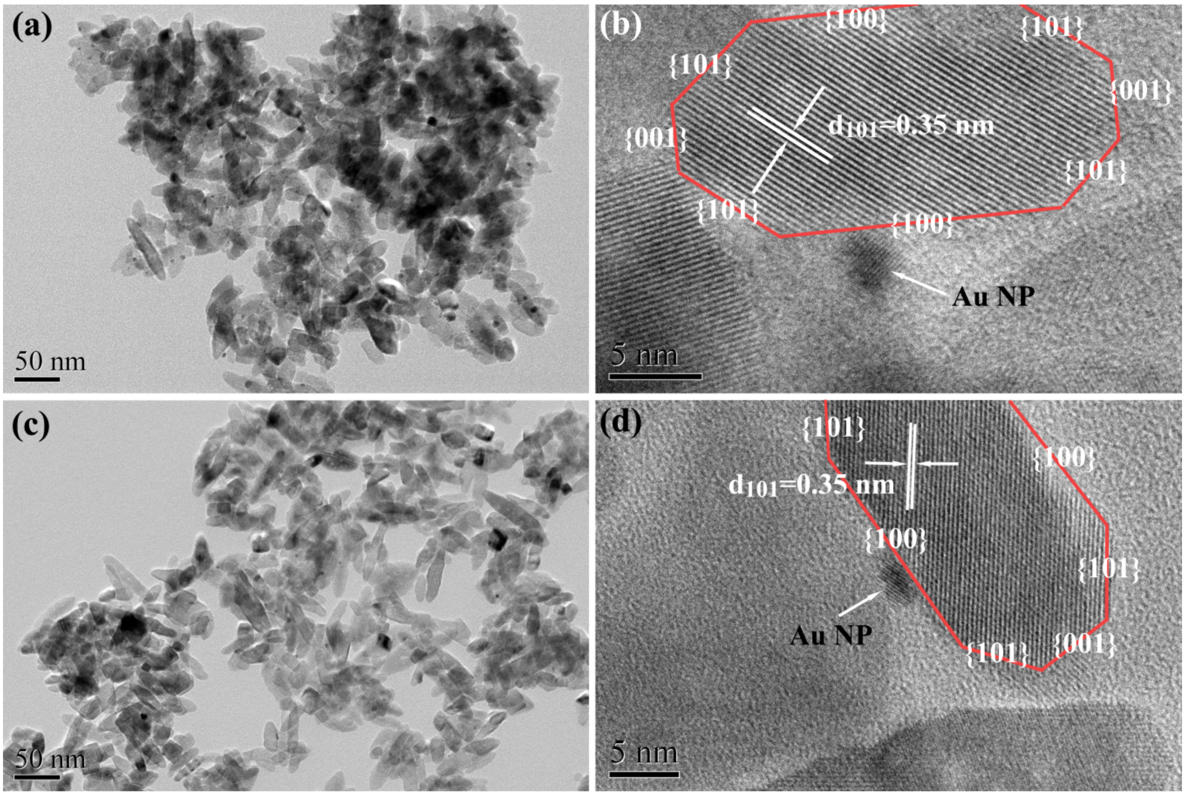

Fig. S4 TEM and HRTEM images of Au/Ti-100 samples after pre-treated in O_2 at 250 °C (a-b) and 300 °C (c-d).

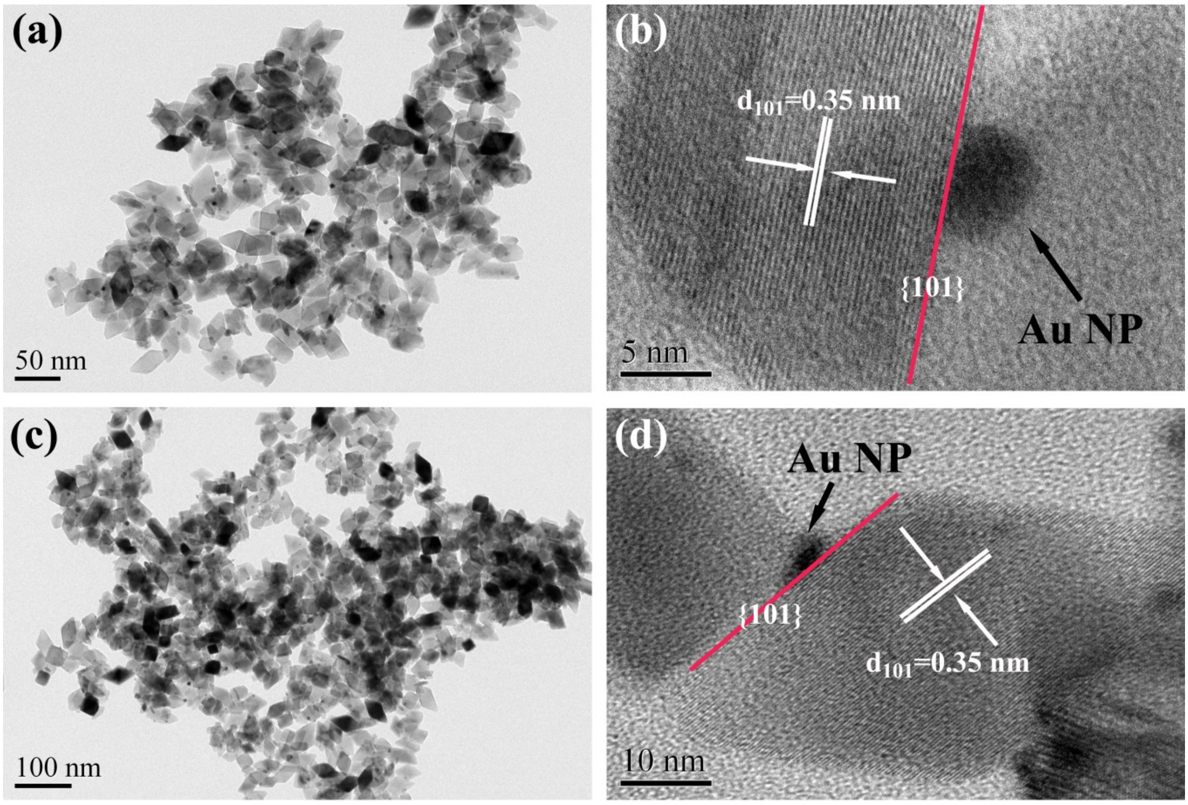

Fig. S5 TEM and HRTEM images of Au/Ti-101 samples after pre-treated in O_2 at 250 °C (a-b) and 300 °C (c-d).

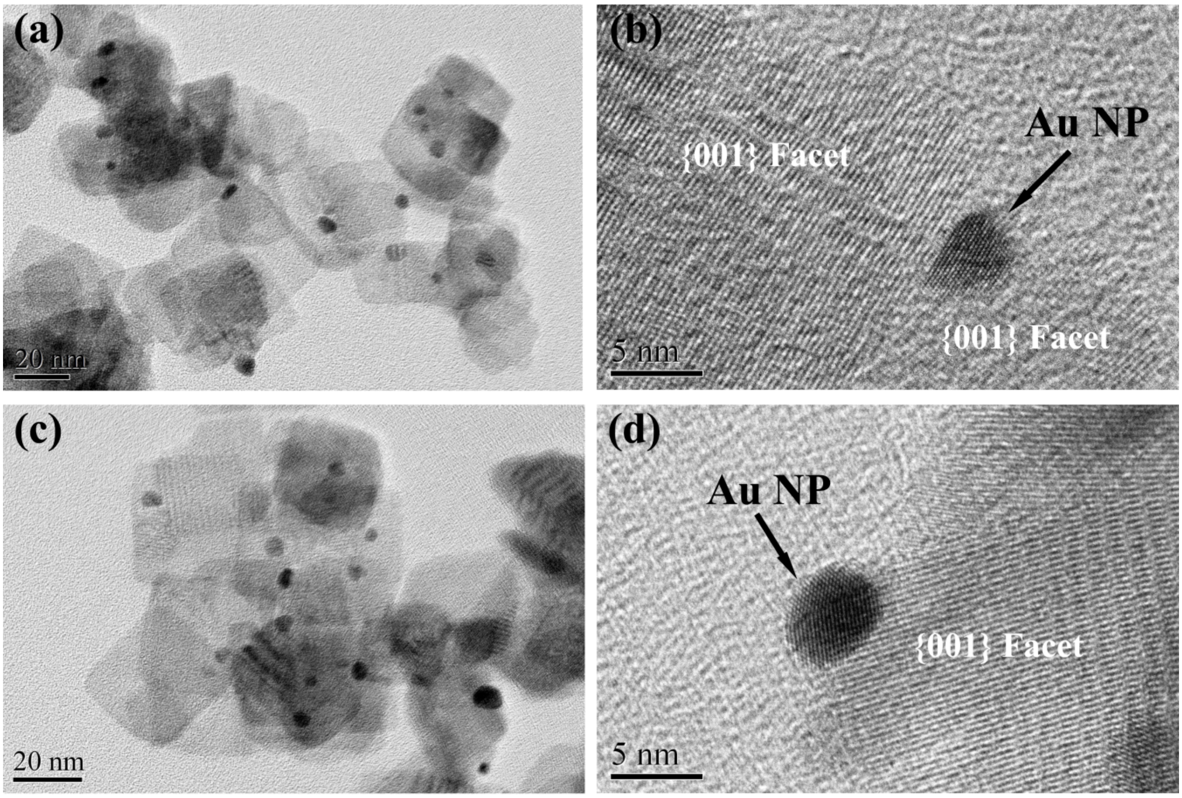

Fig. S6 TEM and HRTEM images of Au/Ti-001 samples after pre-treated in O_2 at 250 °C (a-b) and 300 °C (c-d).

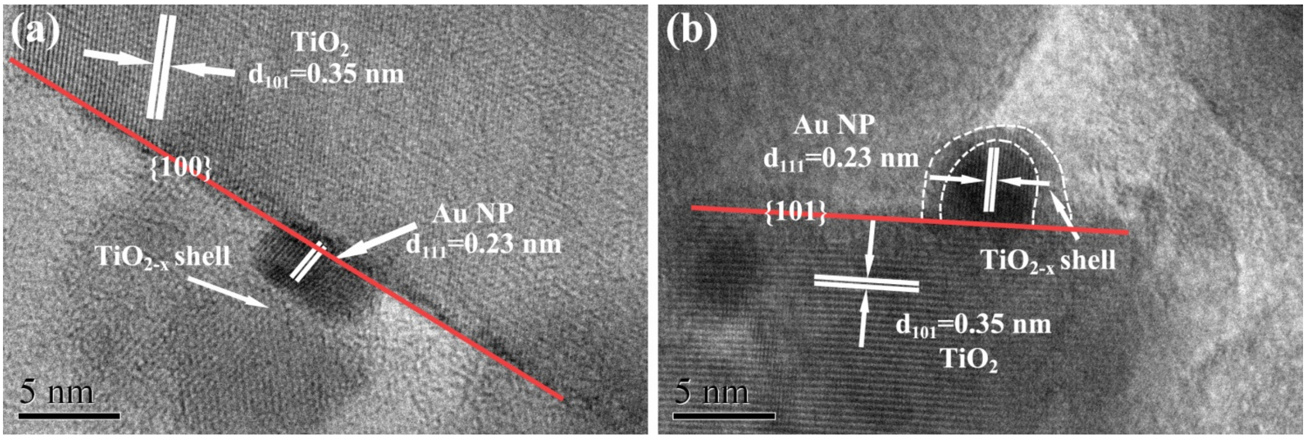

Fig. S7 HRTEM images of Au/Ti-100 (a) and Au/Ti-101 (b) samples after pre-treated in H_2 at 350 °C.

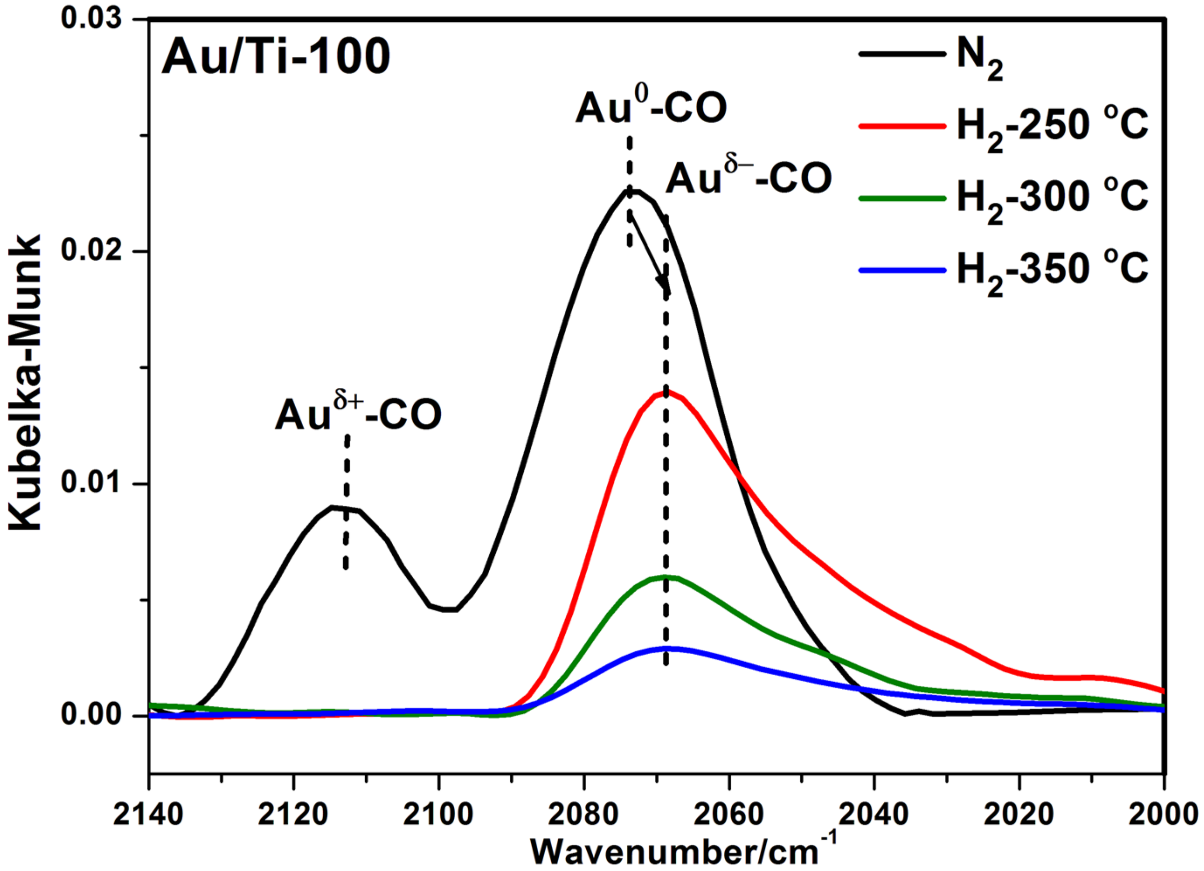

Fig. S8 *In situ* DRIFTS of CO adsorption on Au/Ti-100 after pretreated with H_2 at 250 °C, 300 °C and 350 °C. These spectra are collect when CO is pumped into the reactor for 1 minute.

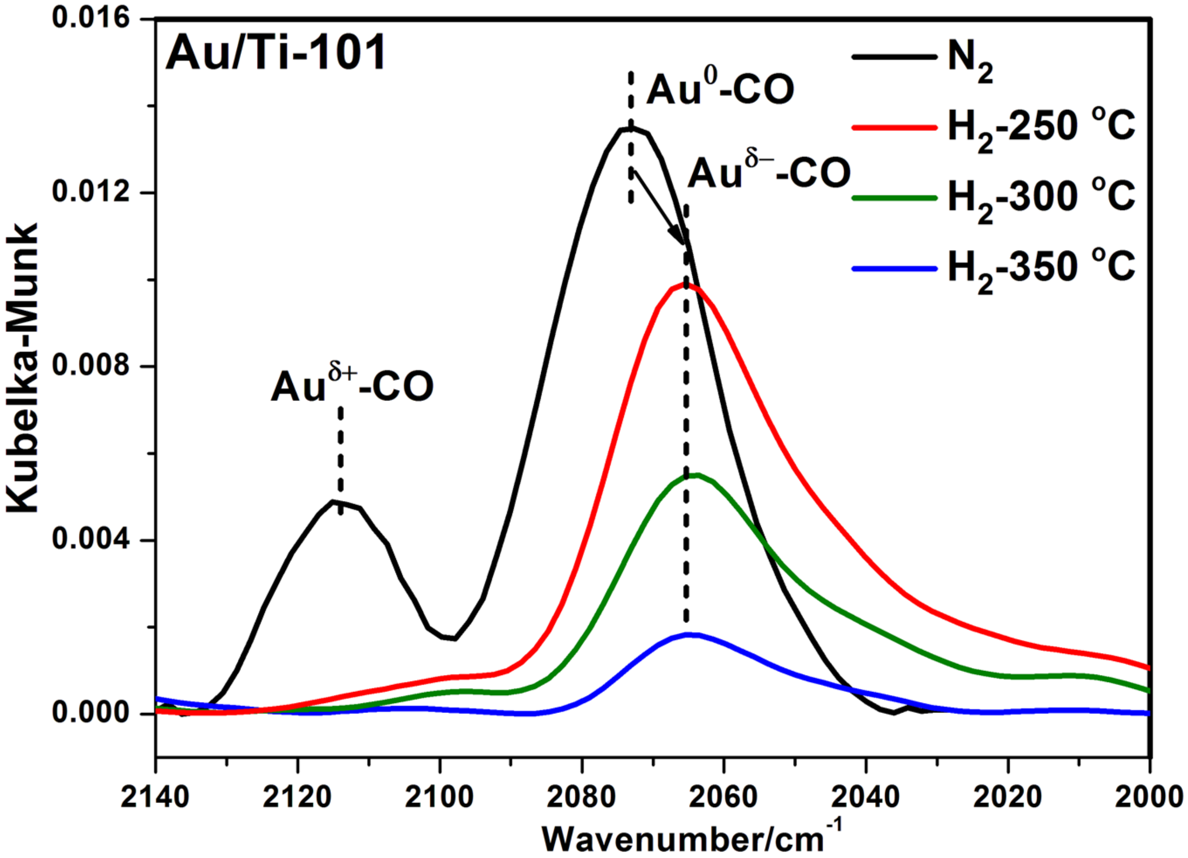

Fig. S9 *In situ* DRIFTS of CO adsorption on Au/Ti-101 after pretreated with H_2 at 250 °C, 300 °C and 350 °C. These spectra are collect when CO is pumped into the reactor for 1 minute.

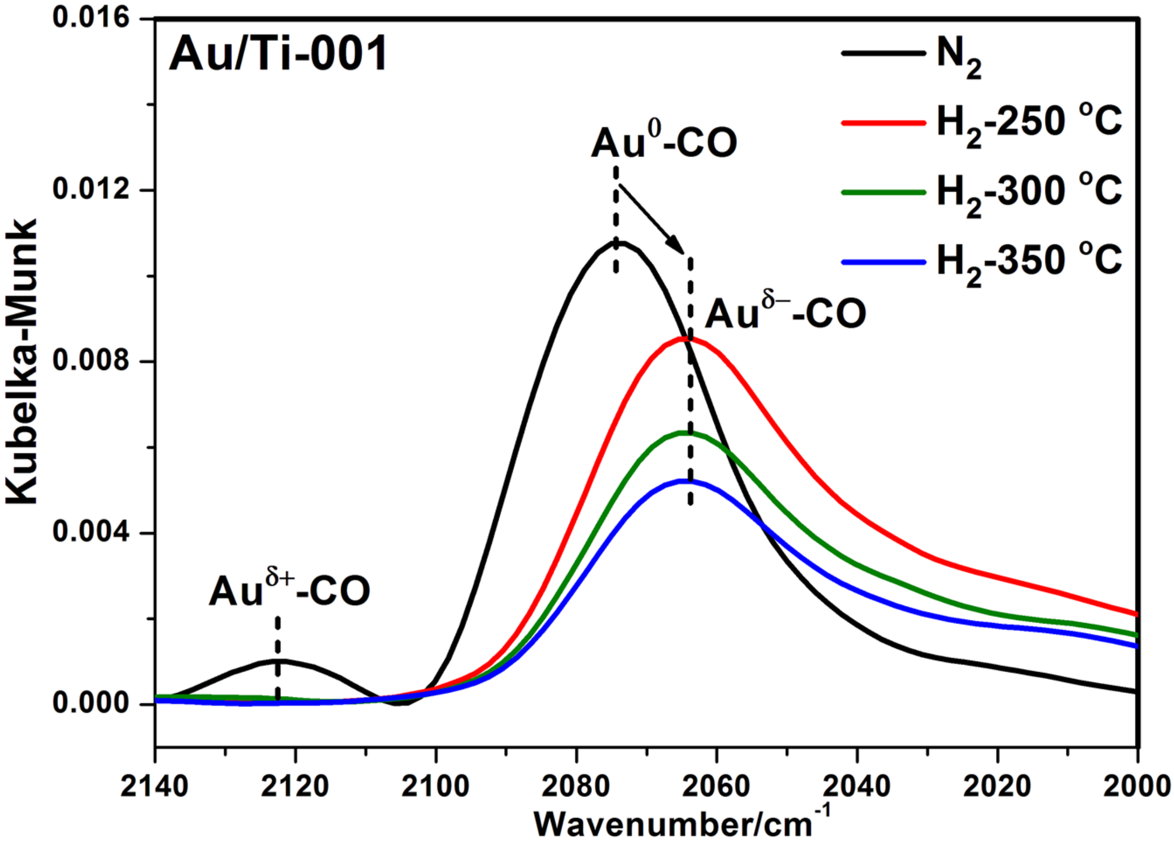

Fig. S10 *In situ* DRIFTS of CO adsorption on Au/Ti-001 after pretreated with H_2 at 250 °C, 300 °C and 350 °C. These spectra are collect when CO is pumped into the reactor for 1 minute.

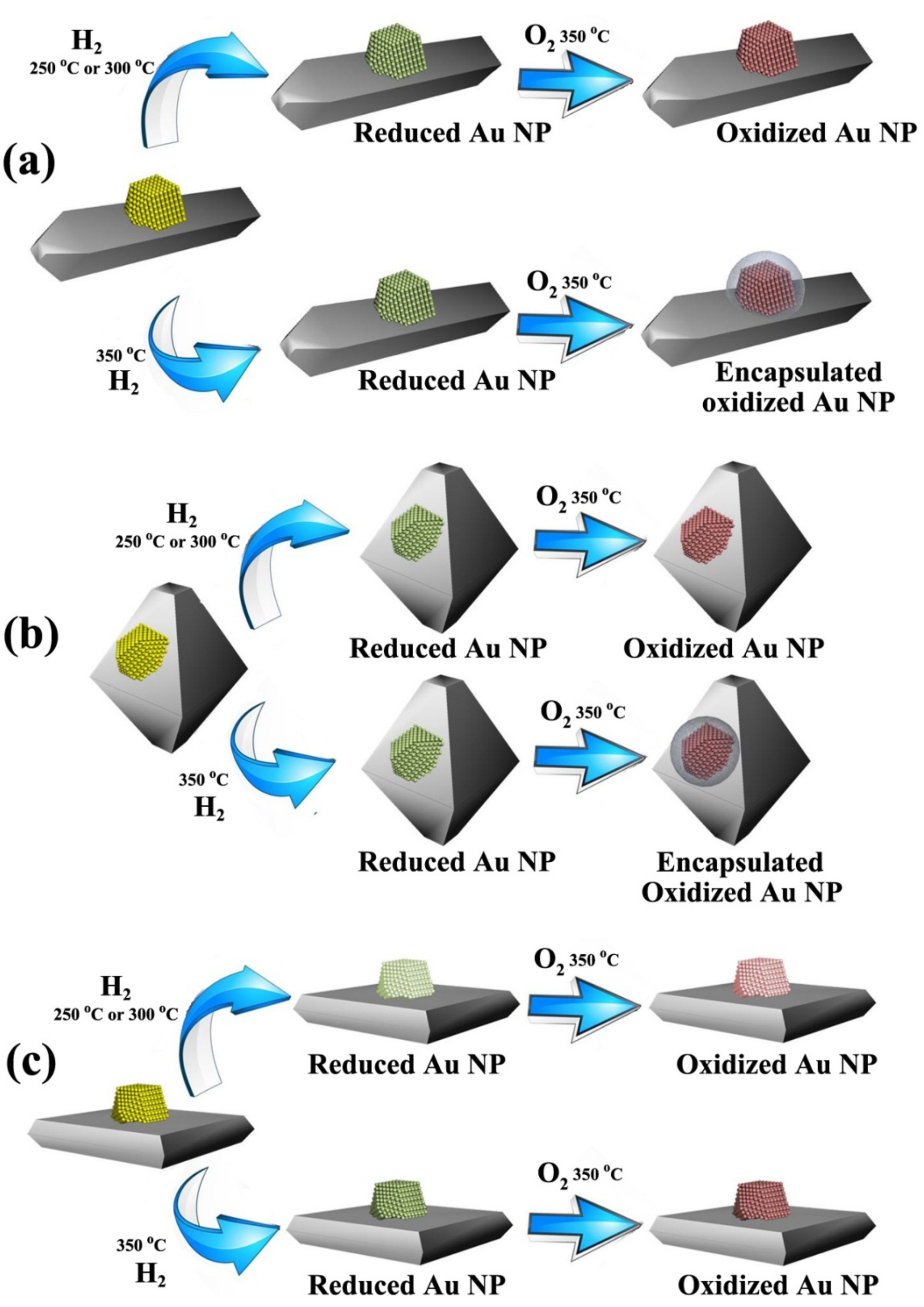

Fig. S11 Schematic illustrations of the structural changes of Au/TiO_2 catalysts with different TiO_2 crystal planes exposed.