Direct Synthesis of Ethanol via CO_2 Hydrogenation Using Supported Gold Catalysts

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Electronic Supplementary Information

1. Chemicals and materials

N,N-dimethylformamide (C_3H_7NO, DMF, 99.8 wt%), N-methyl-2-pyrrolidinone (C_5H_9NO, NMP, 99.5 wt%), cyclohexane (C_6H_{12}, 99.5 wt%), tetrahydrofuran (C_4H_8O, 99 wt%), 1,4-dioxane ($C_4H_8O_2$, 99.5 wt%), titanium tetrachloride ($TiCl_4$, 99.5%), titanium bis (ammonium lactate) dihydroxide aqueous solution (TALH, 50%), urea (99%), chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$, Au≥47.8 wt%), palladium chloride ($PdCl_2$, Pd≥60 wt%), rhodium chloride hydrate ($RhCl_3 \cdot xH_2O$, Rh≥38.5 wt%), chloroplatonic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Pt≥37.5 wt%), and iridium chloride (H_2IrCl_6, Ir≥35.0 wt%) were supplied by Aladdin and used without further purification. 5 wt% Pd/C was purchased from Alfa Aesar. 1 wt% Au/TiO_2 was obtained from Mintek. P25 (TiO_2 with the specific surface area of 45 m^2 g^{-1}, 70% anatase phase and 30% rutile phase) and Al_2O_3 were donated from Evonik.

2. Catalyst preparation

2.1 Preparation of TiO$_2$ polymorphs: The TiO$_2$ with different polymorphs was prepared by hydrothermal or hydrolysis methods following the reported procedure.[S1]

Anatase TiO$_2$ (a-TiO$_2$) was prepared using a hydrothermal method with TALH and urea. The starting materials of 10 mL TALH and 90 mL 0.1 M urea were mixed under stirring at room temperature. The resultant solution was then transferred into a Teflon-lined stainless autoclave, which was sealed and placed in an electric oven held at 160 °C for 24 h. The precipitate was separated by filtration and washed thoroughly with distilled water. After freeze-drying, the solid was obtained and calcined in air at 400 °C for 3 h with a ramp of 2 °C min^{-1}. The amorphous TiO$_2$ (am- TiO$_2$) was prepared in the same way but without calcination.

To prepare brookite TiO$_2$ (b-TiO$_2$), 10 mL TALH and a desired amount of 7 M urea were mixed followed by the addition of distilled water to reach a final volume of 100 mL at room temperature. The resulting solution was transferred into a Teflon-lined stainless autoclave, which was performed in the temperature of 160 °C for 24 h. The precipitate was separated by filtration and washed thoroughly with distilled water. After freeze-drying, the solid was obtained and calcined in air at 400 °C for 3 h with a ramp of 2 °C min^{-1}.

For the synthesis of rutile TiO$_2$ (r-TiO$_2$), TiCl$_4$ was first added dropwise into ethanol, and then the mixture was slowly added to distilled water ($n_{TiCl4}/n_{ethanol}/n_{water}$ = 2/20/280) under stirring at room temperature. After the addition, the solution was further stirred for 30 min, and then was maintained in a closed system at 50 °C in an oven for 24 h. The white precipitate was collected by filtration, and washed with distilled water. After freeze-drying, the solid was obtained and calcined in air at 400 °C for 3 h with a ramp of 2 °C min^{-1}.

2.2 Preparation of 0.3 wt% Au/a-TiO$_2$, 0.3 wt% Au/r-TiO$_2$, 0.3 wt% Au/b-TiO$_2$, 0.3 wt% Au/am-TiO$_2$, and 0.3 wt% Au/TiO$_2$: A deposition−precipitation (DP) procedure has been employed to prepare the Au/TiO$_2$ samples.[S2] Briefly, 1.0 g a-TiO$_2$ (or r-TiO$_2$ or b-TiO$_2$ or am-TiO$_2$ or P25) powder was dissolved with desired amounts of aqueous solution of HAuCl$_4$ (100 mL, 0.25 mM), and the pH was adjusted to 8.0 by dropwise addition of 0.1 M NaOH. After 6 h of stirring at room temperature, the catalyst was separated by filtration and washed five times with distilled water. After freeze-drying, the solid was obtained and followed by a careful reduction with a stream of 5 vol% H$_2$/Ar at 250 °C for 2 h with a ramp of 2 °C min^{-1}. The resulting Au/a-TiO$_2$ (or Au/r-TiO$_2$ or Au/b-TiO$_2$ or Au/am-TiO$_2$ or Au/TiO$_2$) has a gold concentration of 0.3% by weight according to the ICP-AES data.

2.3 Preparation of 0.8 wt% Au/ZrO$_2$: A modified DP procedure has been used to prepare the Au/ZrO$_2$

sample.[S3] 2.0 g ZrO_2 powders were dispersed into 100 mL 1 mM of aqueous solution of $HAuCl_4$, the pH was adjusted to 9.0 by dropwise addition of 0.25 M $NH_3 \cdot H_2O$ (CAUTION: the addition of $NH_3 \cdot H_2O$ to $HAuCl_4$ solution probably give rise to highly explosive fulminating gold). After stirring for 6 h at room temperature, the catalyst was separated by filtration and washed several times with distilled water. The sample was dried at 100 °C in air for 1 h, and followed by a careful reduction treatment with a stream of 5 vol% H_2/Ar at 300 °C for 2 h.

2.4 Preparation of 0.6 wt% Au/Al_2O_3: The Au/Al_2O_3 catalyst was prepared by the DP procedure as described by Iglesia et al.[S4] To obtain the Au/Al_2O_3 catalyst, the pH of the aqueous solution of $HAuCl_4$ was brought to 7.0 by adding NaOH (0.5 M), an appropriate amount of the Al_2O_3 support was added to the neutralized solution, and the resulting suspension was stirred at 80 °C for 1 h. The catalyst precursor was separated from the mother liquor, washed with distilled water, dried in air for 1 day, and calcined in 25 vol% O_2/Ar at 300 °C for 2 h.

2.5 Preparation of 1 wt% Pt/Co_3O_4: The 1 wt% Pt/Co_3O_4 catalyst was prepared by co-precipitation method.[S5] Briefly, 1.5 g $Co(NO_3)_2 \cdot 6H_2O$ and 0.01 g $H_2PtCl_6 \cdot 6H_2O$ were dissolved in 20 mL distilled water, and then the solution was added dropwise to 100 mL Na_2CO_3 solution (0.5 M) in 1 h at room temperature. After stirring for another 1 h, the precipitate was separated by filtration and washed with distilled water. The sample was dried at 100 °C overnight, and followed by calcination at 400 °C for 6 h, and then partly reduced in 5 vol% H_2/Ar at 250 °C for 1 h. Finally, it was subjected to a passivation with 1 vol% O_2/Ar at room temperature for 30 min.

2.6 Preparation of 1 wt% Pd/TiO_2, 1 wt% Ir/TiO_2, 1 wt% Rh/TiO_2, and 1 wt% Au/Co_3O_4: All these catalysts were prepared using the routine incipient wetness technique. Appropriate amount of TiO_2 (P25 or Co_3O_4) was added to the aqueous solution of $PdCl_2$ or H_2IrCl_6 or $RhCl_3 \cdot xH_2O$ or $HAuCl_4 \cdot 4H_2O$. After a perfect mixing of the corresponding slurries and static standing for 12 h, the samples were dried at 100 °C for 12 h, followed by reduction in 5 vol% H_2/Ar at 350 °C for 2 h.

3. Catalyst characterization

3.1 Elemental analysis: The metal loadings of the catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using iCAP 6300 spectrometer.

3.2 BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption–

desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 ^oC prior to acquiring the adsorption isotherm.

3.3 X-ray diffraction (XRD) analysis: The XRD information of the samples was carried out on a German Bruker D8 Advance X-ray diffractometer using nickel filtered Cu Kα radiation at 40 kV and 40 mA.

3.4 Raman analysis: Raman spectra were collected in a Thermal Dispersive Spectrometer using a 10 mW laser with an excitation wavelength of 532 nm.

3.5 X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg Kα, hv = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

3.6 Transmission electron microscopy (TEM): A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images.

3.7 High-resolution transmission electron microscopy (HRTEM): A JEM 2100F electron microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the HRTEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images.

3.8 High-angle annular dark-filed scanning transmission electron microscopy (HAADF-STEM): HAADF-STEM images were obtained on a JEM 2100F electron microscope equipped with a field-emission-gun (FEG) operated at 200 kV and using a HAADF detector. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

3.9 UV–Vis diffuse reflectance (DR) measurements: UV-Vis DR spectra of the solids diluted in $BaSO_4$ were recorded at room temperature on a Shimadzu UV 2401PC Spectrometer equipped with an integrating sphere and using $BaSO_4$ as reference.

3.10 Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements: The DRIFT adsorption experiments were carried out on a Thermo Nicolet 6700 instrument equipped with a MCT detector and Harrick diffuse reflectance accessory. Spectra were obtained on the apparatus loaded with 50 mg of catalyst. Prior to the DRIFT test, sample was subjected to the pretreatment with Helium flow at 200 $^\circ$C for removing any other gases and moisture. Each spectrum was obtained in Helium flow at room temperature and by subtracting the background (base spectrum) of the unpretreated sample.

4. Catalytic activity measurement

The experiments were carried out in high-pressure stainless autoclave reactor (Parr Instrument Co., 4790, 50 mL). Typically, 5 mL solvent (DMF or others) and a known amount of catalyst were placed in the autoclave. The autoclave was sealed and flushed many times with 0.5 MPa CO_2 to remove the air in the reactor, then CO_2 and H_2 gaseous mixtures were charged. The stirrer (800 rpm) was started until the desired temperature was reached. After a certain time, the autoclave was placed in cool water and the gas was carefully released. The gaseous mixture was analyzed using a gas chromatograph Agilent 7820A equipped with a TDX-01 column connected to a thermal conductivity detector. A known amount of internal standard 1, 4-dioxane was added into the aqueous product in autoclave. The reaction mixture was transferred into a centrifuge tube and the solid catalyst was separated by centrifugation. The product solution was quantitatively analyzed using a gas chromatograph Agilent 7820A equipped with a HP-5 capillary column connected to a flame ionization detector. Identification of the products was performed by using a GC-MS spectrometer. Noted that the total carbon balance was > 95%. For the catalyst recycling experiment, the centrifuged catalysts were collected and washed with distilled water several times, followed by freeze-drying for 12 h and a careful reduction with a stream of 5 vol% H_2/Ar at 250 °C for 2 h with a ramp of 2 $^\circ$C min^{-1}.
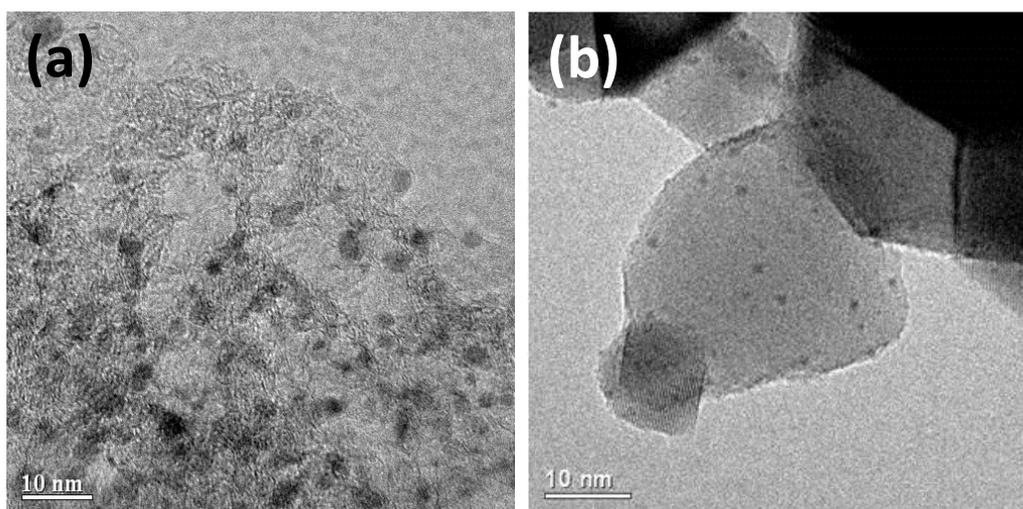
Fig. S1 TEM images of (a) Pd/C and (b) Ir/TiO$_2$.
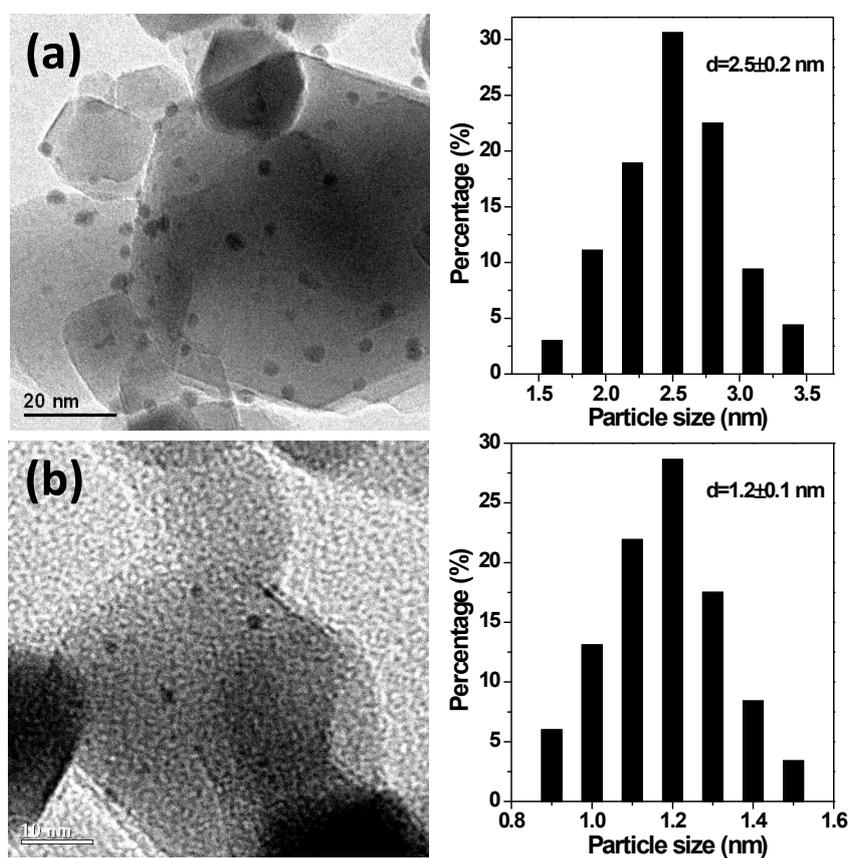
Fig. S2 TEM images and the corresponding Au particle size distributions of (a) Mintek Au/TiO$_2$ and (b) 0.3 wt% Au/TiO$_2$.
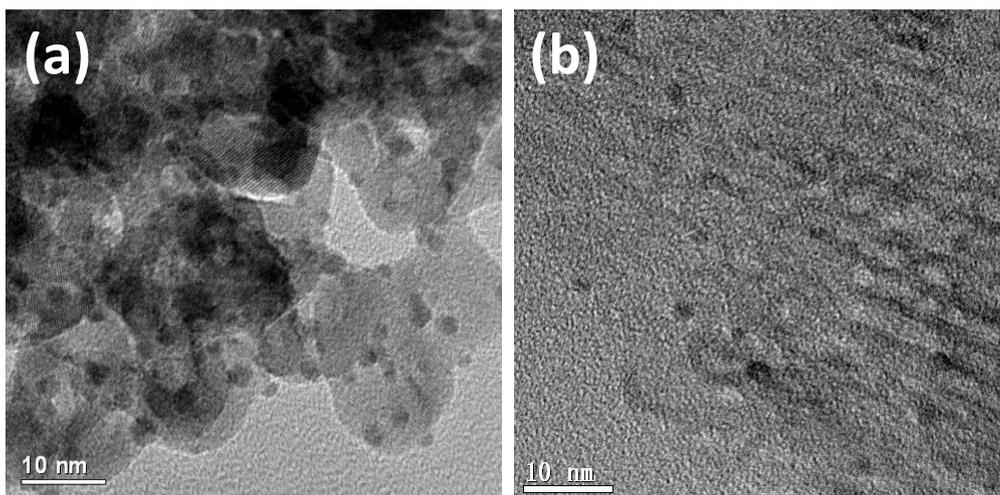
Fig. S3 TEM images of (a) Au/ZrO$_2$ and (b) Au/Al$_2$O$_3$.
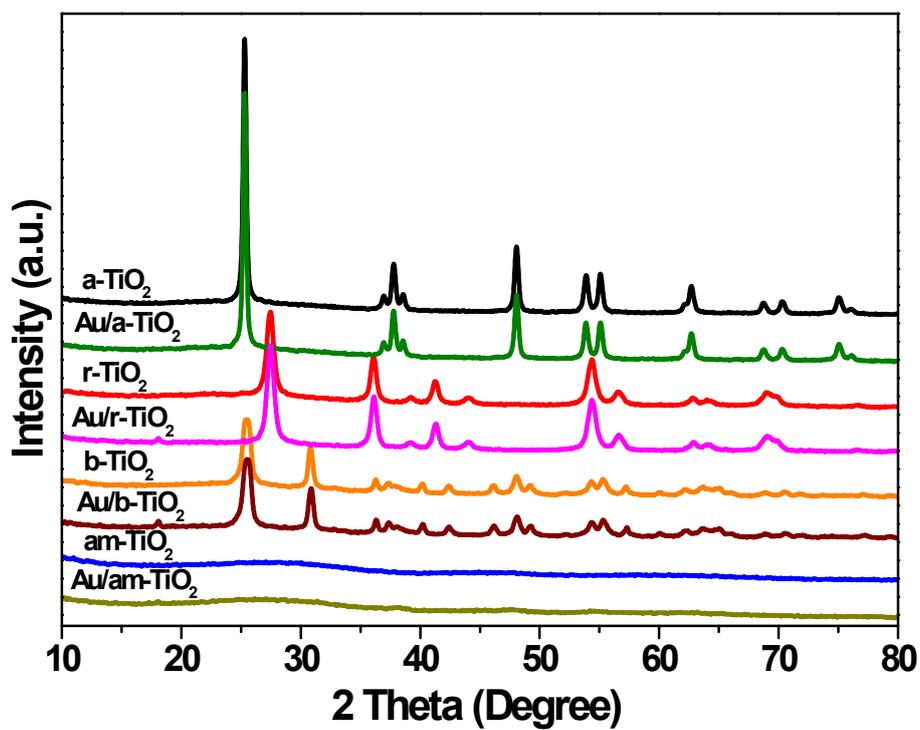
Fig. S4 XRD patterns of a-, r-, b-, am-TiO$_2$, and their supported Au catalysts.

Table S1 BET surface area of TiO$_2$ with different polymorphs.

Sample	Surface area (m^2 g^{-1})
a-TiO$_2$	58.2
r-TiO$_2$	47.8
b-TiO$_2$	79.3
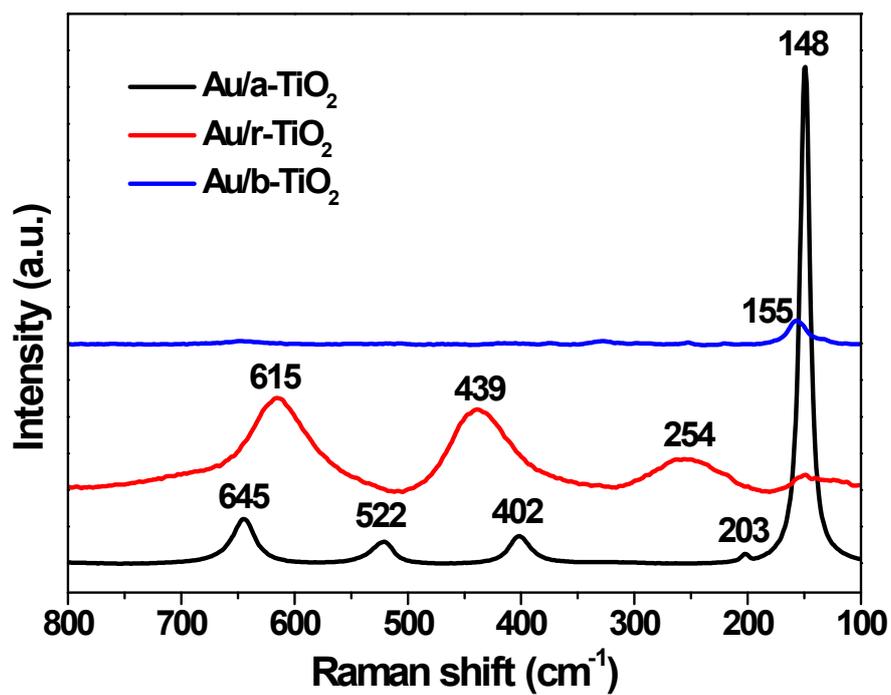
Fig. S5 Raman spectra of a-, r-, and b-TiO$_2$ supported Au catalysts.
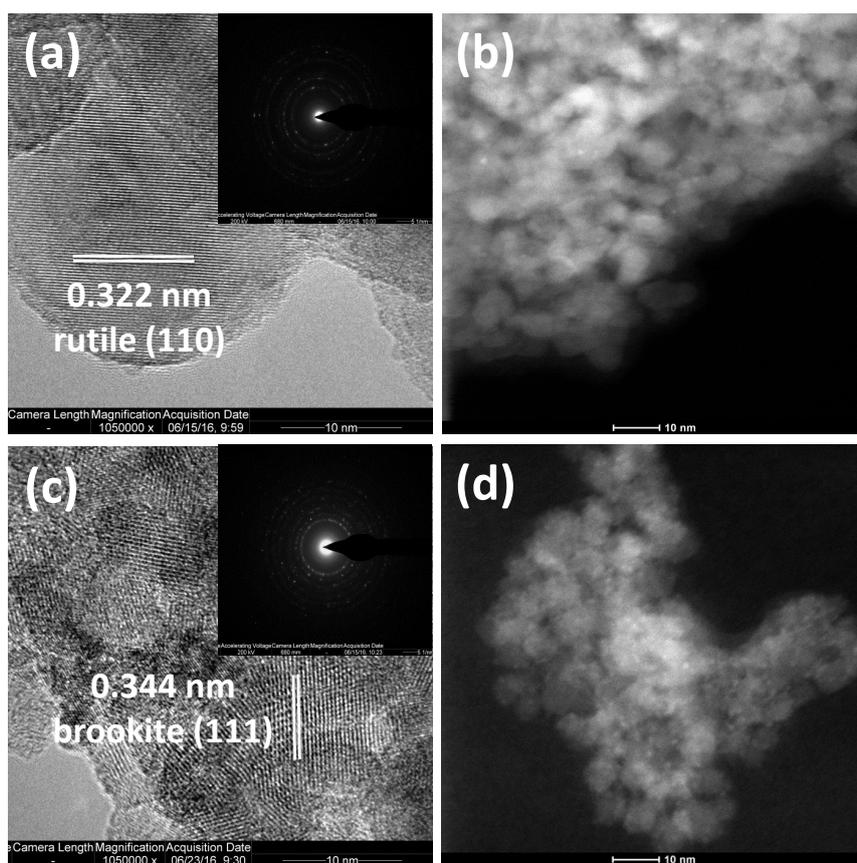
Fig. S6 HRTEM images (insets show the corresponding SAED patterns) of (a) r-TiO$_2$ and (c) b-TiO$_2$, and

HAADF-STEM images of (b) Au/r-TiO$_2$ and (d) Au/b-TiO$_2$ catalysts.
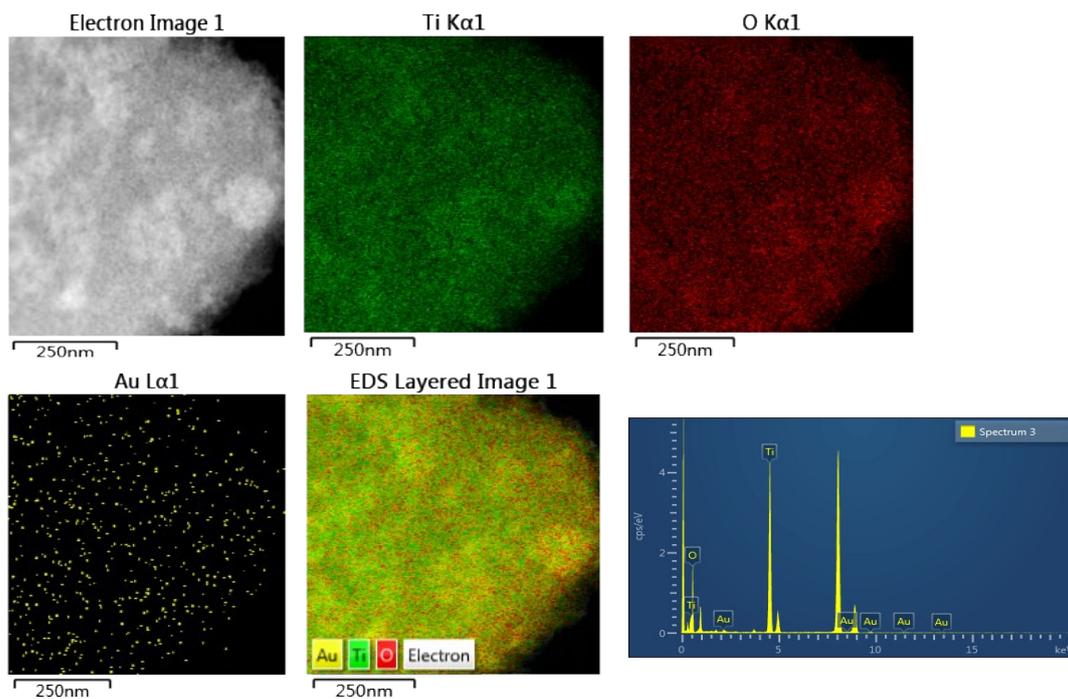
Fig. S7 STEM-EDS mappings and EDS spectrum of Au/a-TiO$_2$.
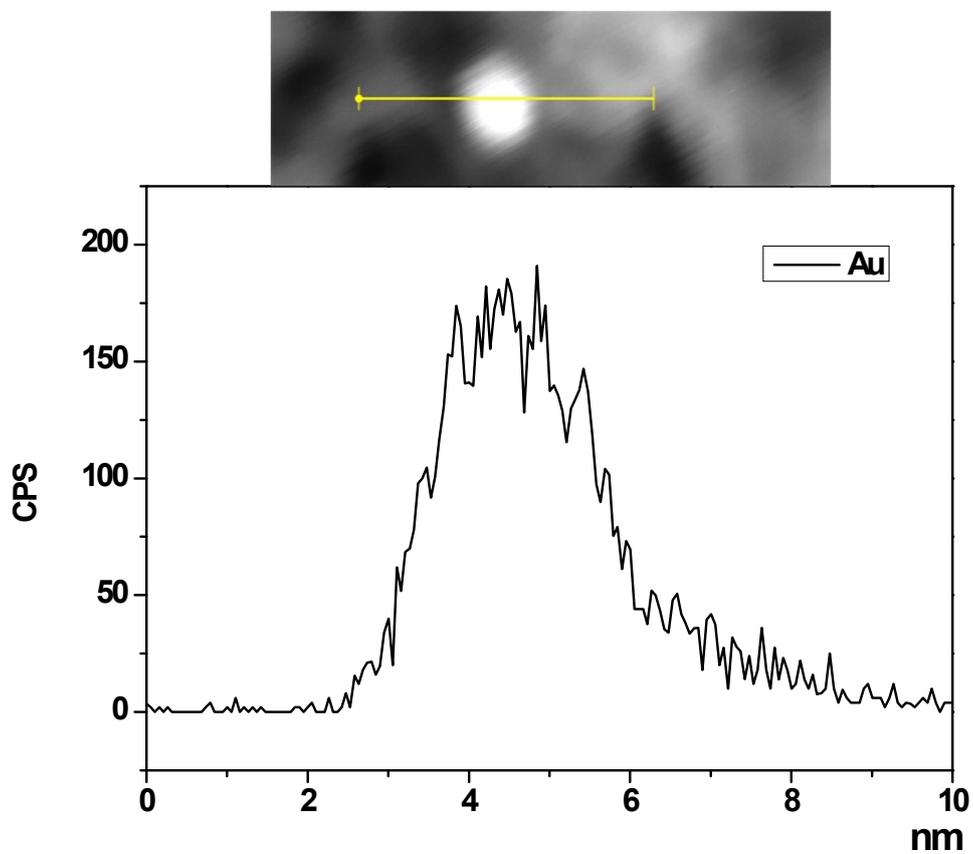
Fig. S8 STEM/EDS spectrum with Au line amplified of Au/a-TiO$_2$.
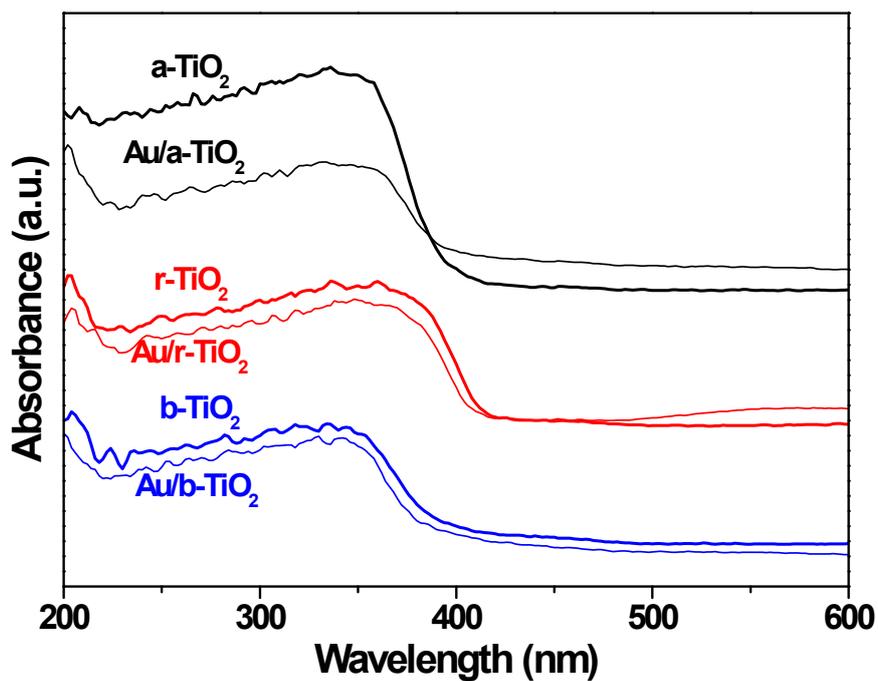
Fig. S9 UV−visible diffuse reflectance spectra of a-, r-, b-TiO$_2$, and their supported Au catalysts.

Table S2 Band gap of a-, r-, b-TiO$_2$, and their supported Au catalysts.

Sample	Band gap (eV)[a]
a-TiO$_2$	3.15
Au/a-TiO$_2$	3.16
r-TiO$_2$	3.01
Au/r-TiO$_2$	3.04
b-TiO$_2$	3.10
Au/b-TiO$_2$	3.11

[a] The band gap was calculated based on the equation $E_g = hc/\lambda_g$,[S6] where h is the Planck's constant, c is the speed of light in vacuum, and λ_g is the wavelength. Replacing the values for h and c the relation become: $E_g = 1240/\lambda_g$. And the values with an error of ±1% can be detected.
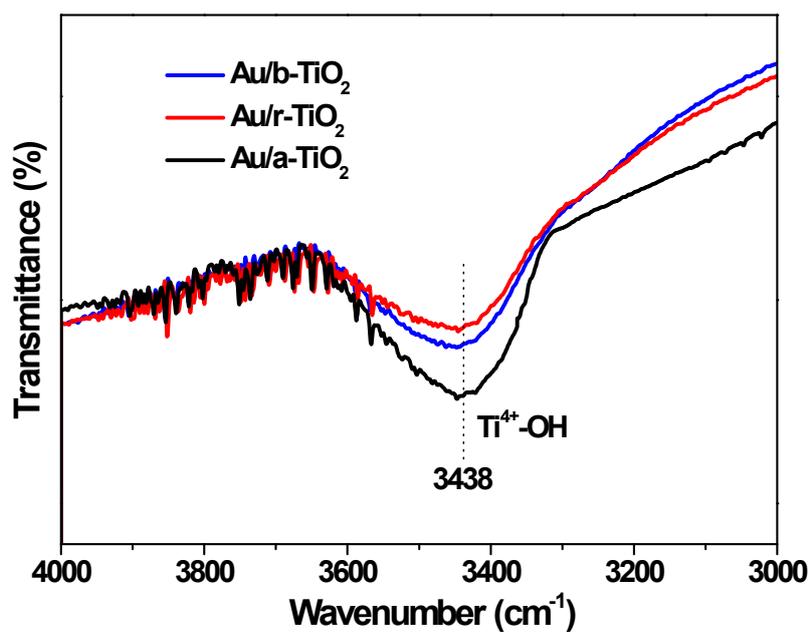
Fig. S10 DRIFT spectra of a-, r-, and b-TiO$_2$ supported Au catalysts. The band of 3438 cm^{-1} was assigned to the stretching vibration of H-bound OH groups in Ti^{4+}−OH (oxygen vacancies).
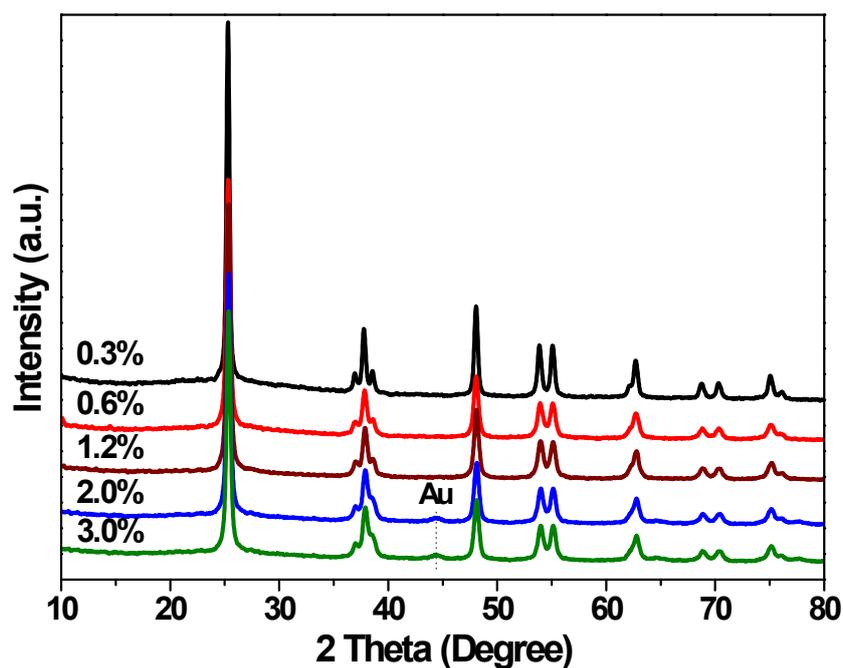
Fig. S11 XRD patterns of Au/a-TiO$_2$ catalysts with different Au loadings.
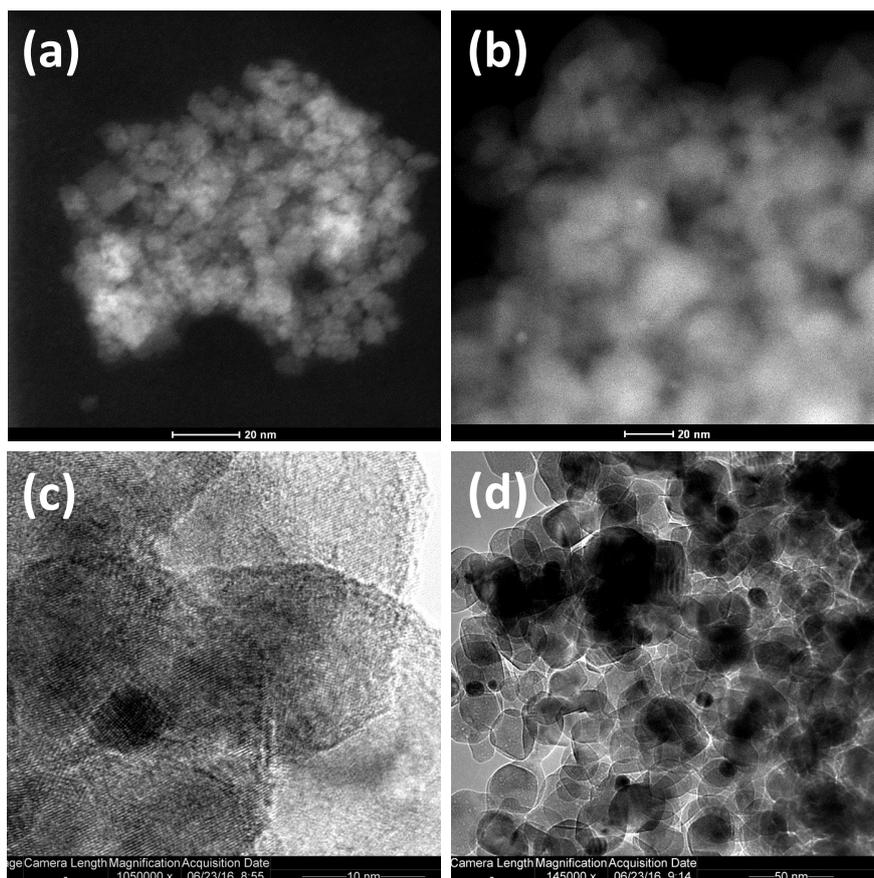
Fig. S12 HAADF-STEM images of (a) 0.6 wt% Au/a-TiO$_2$ and (b) 1.2 wt% Au/a-TiO$_2$, and HRTEM images of (c) 2.0 wt% Au/a-TiO$_2$ and (d) 3.0 wt% Au/a-TiO$_2$ catalysts. The average Au particle size was 1.4 ± 0.1 nm, 2.8 ± 0.2 nm, 5.2 ± 0.4 nm, and 8.1 ± 1.0 nm for (a) to (d), respectively.

Table S3 Synthesis of EtOH from MeOH, CO, and H$_2$ using Au/a-TiO$_2$.

Entry	n_{EtOH} (mmol)	STY of EtOH (mmol g$_{Au}^{-1}$ h^{-1})
1[a]	3.1	1036.7
2[b]	3.4	1137.1

[a] 100 mg Au/a-TiO$_2$, 5 mL MeOH, 45 bar H$_2$ and 15 bar CO at 25 °C, 200 °C, 10 h. [b] 100 mg Au/a-TiO$_2$, 5 mL MeOH, 40 bar H$_2$ and 20 bar CO at 25 °C, 200 °C, 10 h.
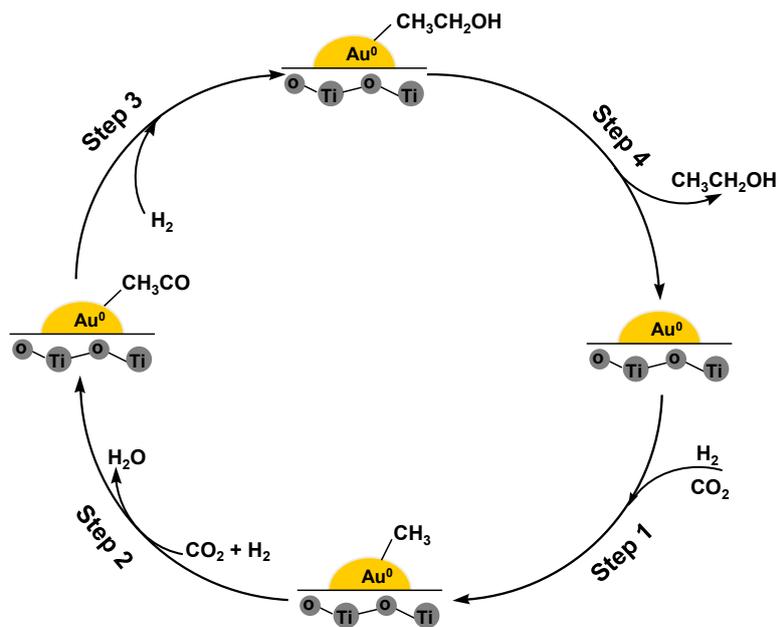
Scheme S1 Possible reaction pathway for EtOH synthesis from CO_2 and H_2 over Au/a-TiO_2 catalyst.
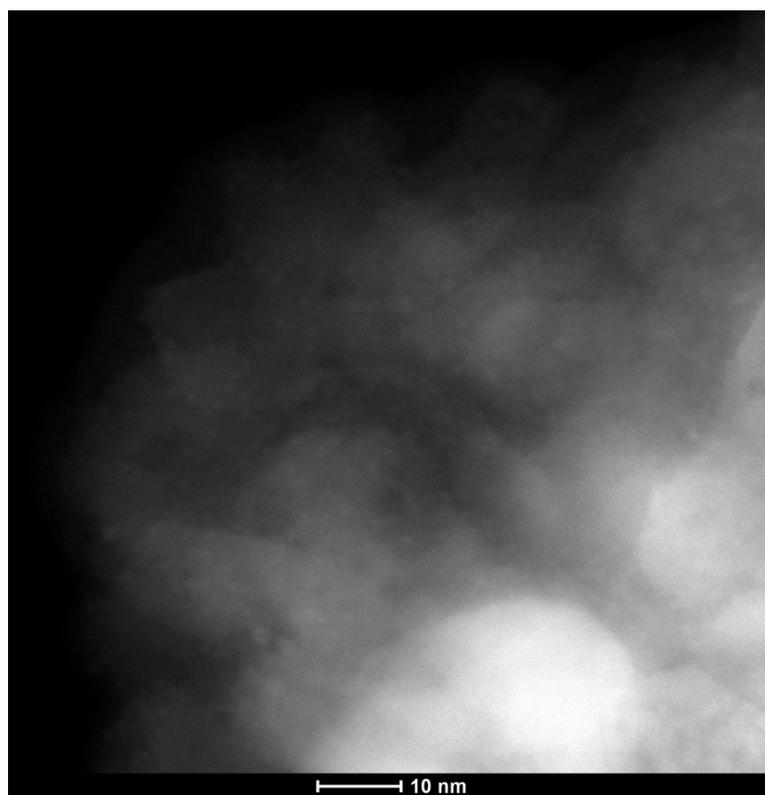
Fig. S13 HAADF-STEM image of the used Au/a-TiO_2 catalyst.

References

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