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Electronic Supporting Information

Catalytic Mechanism of Heterogeneous Au Nanoparticles towards Low-Temperature Water-Gas Shift Reaction

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Experimental section

1. Preparation of ZnTi-MMO. The preparation of ZnTi-LDHs precursor with $[Zn^{2+}]/[Ti^{4+}]$ = 2/1 was similar to the method reported by our group.[1] After a calcination in the muffle furnace at 500 °C for 4 h, ZnTi-LDHs precursor transformed to zinc-titanium mixed metal oxide (ZnTi-MMO).

2. Preparation of Au@TiO_{2-x}/ZnO(H300). Au samples were prepared *via* a deposition-precipitation method with urea. Typically, 1.0 g of ZnTi-MMO was added to 100 mL of $HAuCl_4$ (1.20×10^{-3} M) and urea (0.42 M) mixed aqueous solution. The suspension was heated at 90 °C with vigorous stirring for 4 h, and the resulting precipitation was filtered, centrifugal washing with deionized water thoroughly to eliminate Cl^- and dried in vacuum at 60 °C for 4 h. Subsequently, the obtained Au/ZnTi-MMO was pretreated in a H_2/N_2 stream (4:6, v/v) for 2 h at 300 °C (heating rate: 5 °C min^{-1}), followed by cooling to 25 °C in a high purity N_2 stream. The obtained samples were denoted as Au@TiO_{2-x}/ZnO(H300).

3. *In situ/operando* DRIFTS experiments. *In situ* and *operando* diffuse reflectance Fourier transform infrared spectroscopy (*in situ/operando* DRIFTS) was carried out in an *in situ* reaction cell on a Bruker TENSOR II spectrometer equipped with a MCT narrow-band detector. The detailed pre-treatment and test conditions are given as follows:

(1) *In situ* DRIFT spectra with the introduction of various reagents (CO or H_2O) at 200 °C: prior to the test, the catalyst was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) for 30 min and cooling to 200 °C. Subsequently, H_2O vapor was introduced into the *in situ* reaction cell *via* a HPLC pump, and the DRIFT spectra were collected within 10 min. Afterwards, a high

purity He (50 mL min^{-1}) was purged for 30 min, followed by a switch to CO/He (v/v, 1:19) atmosphere for the collection of DRIFT spectra for another 10 min (as shown in Fig. 2).

(2) *Operando* DRIFT spectra with the introduction of reaction atmosphere (6% CO, 25% H_2O and 69% He) at 200 °C: the catalyst was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) for 30 min and cooling to 200 °C. Subsequently, a mixture of CO, H_2O and He (6% CO, 25% H_2O and 69% He) was introduced into the reaction cell with a total flux of 100 ml min^{-1}, and the DRIFT spectra were collected within 20 min (as shown in Fig. 5).

(3) *In situ* DRIFT spectra with the introduction of H_2O vapor at different temperatures: the catalyst was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) for 30 min and cooling to 100 ºC, 150 ºC, 200 ºC, 250 ºC, and 300 ºC, respectively. Subsequently, H_2O vapor was introduced into the *in situ* reaction cell *via* a HPLC pump and maintained for 10 min at different temperatures. Then, a high purity He (50 mL min^{-1}) was purged was purged for 30 min and the temperature was decreased to 25 °C. Finally, a switch to CO/He (v/v, 1:19) atmosphere was performed for the collection of DRIFT spectra for 30 min (as shown in Fig. S6).

4. XAS characterizations. *In situ/operando* extended X-ray absorption fine structure spectroscopy (EXAFS) at the Au L_3-edge and Ti K-edge was carried out at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The typical energy of the storage ring was 2.5 GeV with a maximum current of 250 mA. The Si (111) double crystal monochromator was used. The powdered sample was first pressed into a thin round sheet with a diameter of 13 cm and placed into an *in situ* reaction cell equipped with polyimide windows. The detailed experiment procedure is described as follows:

(1) *In situ* EXAFS spectra at Au L_3-edge with the introduction of various reagents (CO or H_2O) at 200 °C: The catalyst was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) for 30 min and cooling to 200 °C, and then EXAFS spectra at Au L_3-edge were collected. Subsequently, H_2O vapor was introduced into the *in situ* reaction cell *via* a HPLC pump, and Au L_3-edge EXAFS spectra were collected within 30 min. Finally, a switch to CO/He (v/v, 1:19) atmosphere was performed for the collection of Au L_3-edge EXAFS spectra for another 30 min (as shown in Fig. 4a).

(2) *Operando* EXAFS spectra at Au L_3-edge: The sample was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) 30 min and cooling to 200 °C, and then EXAFS spectra at Au L_3-edge were collected. Subsequently, a mixture of CO, H_2O and He (6% CO, 25% H_2O and 69% He) was introduced into the reactor with a total flux of 100 ml min^{-1}, and then Au L_3-edge EXAFS spectra were collected under stable *operando* conditions at 200 °C for 20 min (as shown in Fig. 6a).

(3) *In situ* EXAFS spectra at Ti *K*-edge with the introduction of various reagents (CO or H_2O) at 200 °C: The catalyst was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) 30 min and cooling to 200 °C, and then EXAFS spectra at Ti *K*-edge were collected. Subsequently, H_2O vapor was introduced into the *in situ* reaction cell *via* a HPLC pump, and Ti *K*-edge

EXAFS spectra were collected within 30 min. Finally, a switch to CO/He (v/v, 1:19) atmosphere was performed for the collection of Ti *K*-edge EXAFS spectra for another 30 min (as shown in Fig. 4b).

(4) *Operando* EXAFS spectra at Ti *K*-edge: The sample was firstly reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) for 30 min and cooling to 200 °C, and then EXAFS spectra at Ti *K*-edge were collected. Subsequently, a mixture of CO, H_2O and He (6% CO, 25% H_2O and 69% He) was introduced into the reactor with a total flux of 100 ml min^{-1}, and then Ti *K*-edge EXAFS spectra were collected under stable *operando* conditions at 250 °C for 20 min (as shown in Fig. 6b).

5. *In situ* H_2O Pulse TPD-MASS and cycling tests of H_2O and CO Pulse-MASS. *In situ* H_2O Pulse TPD-MASS and *in situ* cycling tests of H_2O and CO Pulse TPD-MASS were performed on a Micromeritics ChemiSorb 2070 with a thermal conductivity detector (TCD). The detailed experimental process is given as follows: In a typical process, ~50 mg of sample was sealed in a quartz tube reactor and reduced in a H_2/He (v/v, 1:19) stream at 300 °C for 2 h at a heating rate of 5 °C min^{-1}, followed by flowing a high purity He (50 mL min^{-1}) for 30 min and cooling to 100 ºC, 150 ºC, 200 ºC, 250 ºC, and 300 ºC, respectively. Finally, pulse water was introduced with a time interval of 5 min (cycle times: 10), and the Mass signals for H_2 and H_2O were collected during the water pulsing (as shown in Fig. 3a–e). As for the cycling tests of H_2O and CO Pulse-MASS measurements, after the reduction process in H_2 atmosphere and flushing with He for 30 min, water pulse was induced into the reactor for 2 min at 300 ºC, followed by the input of CO pulse for another 2 min. The cycle pulse atmosphere was H_2O, CO, H_2O, CO in sequence for 15−20 cycles. The Mass signals for H_2 , H_2O CO and CO_2 were collected during the water flowing (as shown in Fig. 3f).

6. DFT calculations details. Quantum mechanical calculations were carried out by employing the DFT method provided in the Vienna ab initio simulation package (VASP).[2,3] The exchange-correlation potential was depicted by the Perdew-Burke-Ernzerh (PBE) of generalized gradient approach (GGA).[4,5] The projector augmented wave (PAW) potentials were used to describe the core electrons.[6,7] k-point sampling (3×3×1) in the surface Brillouin zone and an energy cutoff of 400 eV were applied.[8] Spin polarization was taken into account for all models in the calculations. The converge criteria of the force on each relaxed atom was set to 0.05 eV $Å^{-1}$. The tolerance of energy convergence was 1×10^{-5} eV. The space between neighboring slabs was filled with a vacuum region of 10 Å along the direction perpendicular to the surface. Transition state (TS) searches were carried out with the CI-NEB method[9]

The adsorption energy (E_{ads}, as shown in Fig. 6c, d) was calculated by the electronic energy difference between the surface containing adsorbate (E_{total}) and the clean surface plus the free molecule in gas phase ($E_{slab}+E_g$),

$$E_{ads} = E_{total} - (E_{slab}+E_g) \qquad (1)$$

The activation barrier (E_a, as shown in Fig. 7) was obtained from the electronic energy difference between the transition state (E_{TS}) and its corresponding initial state (E_{IS}), which was defined as:

$$E_a = E_{TS} - E_{IS} \qquad (2)$$

According to the ac-HAADF-STEM observations, Au/TiO_2(101) was built by a slab of TiO_2 and a supported Au_6 cluster on its surface. TiO_2(101) surface was represented by p (2×3) supercell with three layers, of which the two bottom layers were constrained during the calculation, while the top layer was fully relaxed to participate in reactions. One O_{2c} atom was removed to produce oxygen vacancy (O_v) in Au/TiO_{2-x}(101) system, because O_{2c} is exposed on the outermost surface of the model.

According to the experimental results, the path of WGSR in the model system obeys the redox mechanism, which consists of six steps: reactants adsorption (R1 and R2), first-step H_2O dissociation (R3), second-step H_2O dissociation (R4), H_2 formation (R5), CO oxidation (R6) and products desorption (R7 and R8).

$$CO + * \leftrightarrow CO* \qquad (R1)$$

$$H_2O + * \leftrightarrow H_2O* \qquad (R2)$$

$$H_2O* + * \leftrightarrow OH* + H* \qquad (R3)$$

$$OH* + * \leftrightarrow H* + O* \qquad (R4)$$

$$2H* \rightarrow H_2* + * \qquad (R5)$$

$$CO* + O* \rightarrow CO_2 * + * \qquad (R6)$$

$$CO_2* \rightarrow CO_2(g) + * \qquad (R7)$$

$$H_2* \rightarrow H_2(g) + * \qquad (R8)$$

where the "*" represents a surface site; "X*" represents the binding of adsorbate to the site.

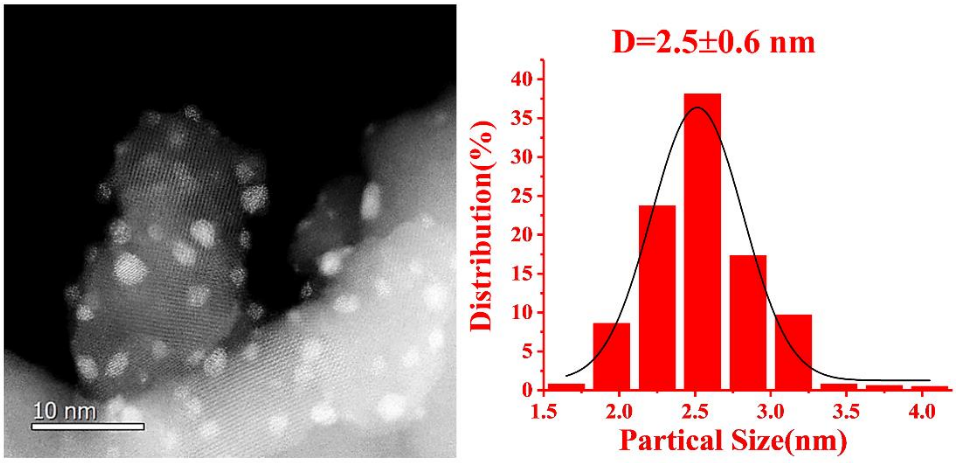

Fig. S1. Ac-HAADF-STEM image of the Au@TiO$_{2-x}$/ZnO(H300) sample and the corresponding size distribution of Au NPs. The size distribution was obtained by analyzing about 200 Au NPs from STEM image.

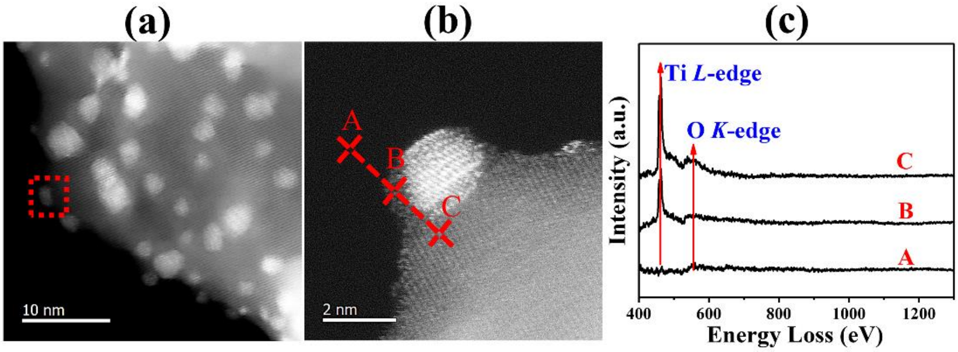

Fig. S2. (a) Ac-HAADF-STEM image of the Au@TiO$_{2-x}$/ZnO(H300) sample; (b) high resolution ac-HAADF-STEM image in panel a; (c) EELS collected at Spot A, B, C, respectively.

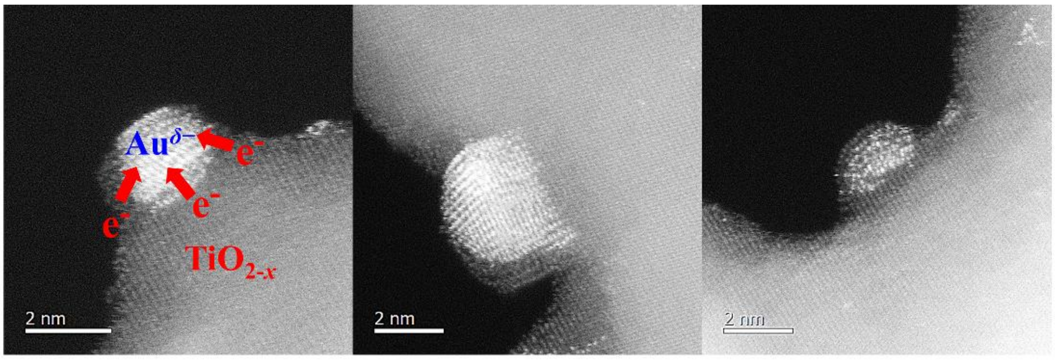

Fig. S3. High resolution ac-HAADF-STEM images of the Au@TiO$_{2-x}$/ZnO(H300) sample.

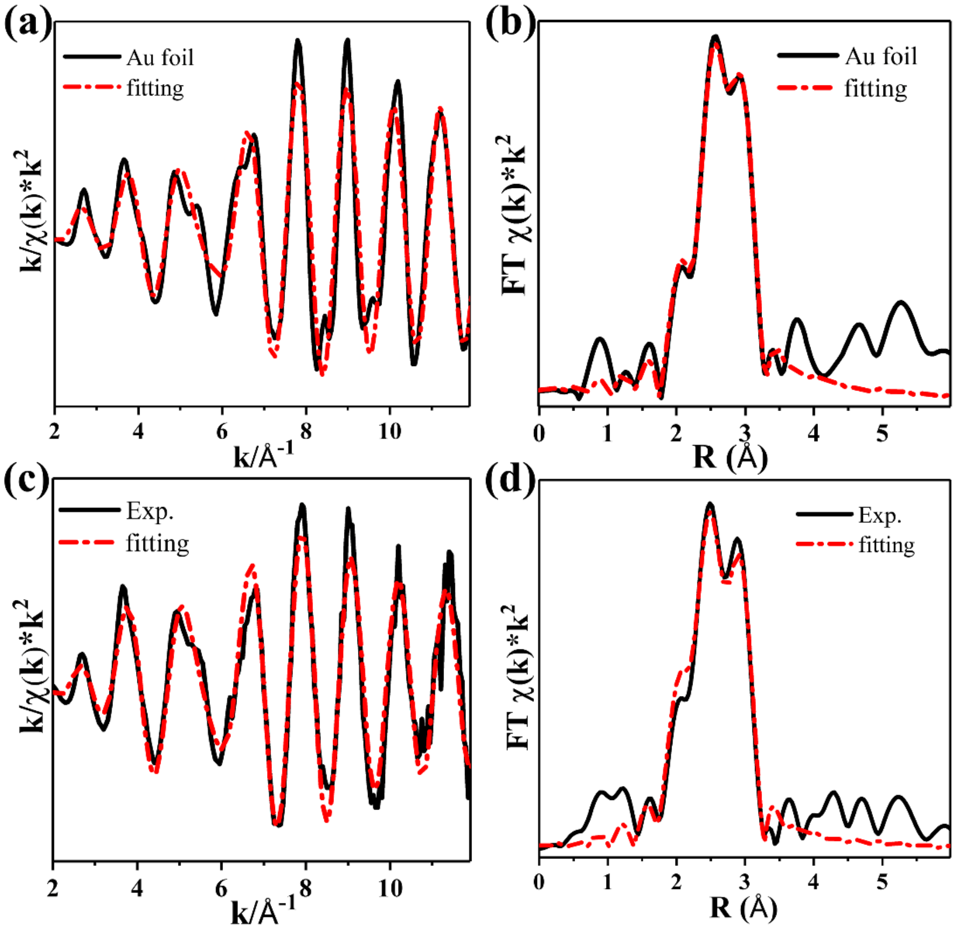

Fig. S4. Au L_3 edge EXAFS spectra and fitting results of (a) Au foil k-space, (b) Au foil R-space, (c) Au@TiO_{2-x}/ZnO(H300) k-space and (d) Au@TiO_{2-x}/ZnO(H300) R-space. The quantified fitting results are listed in Table S2.

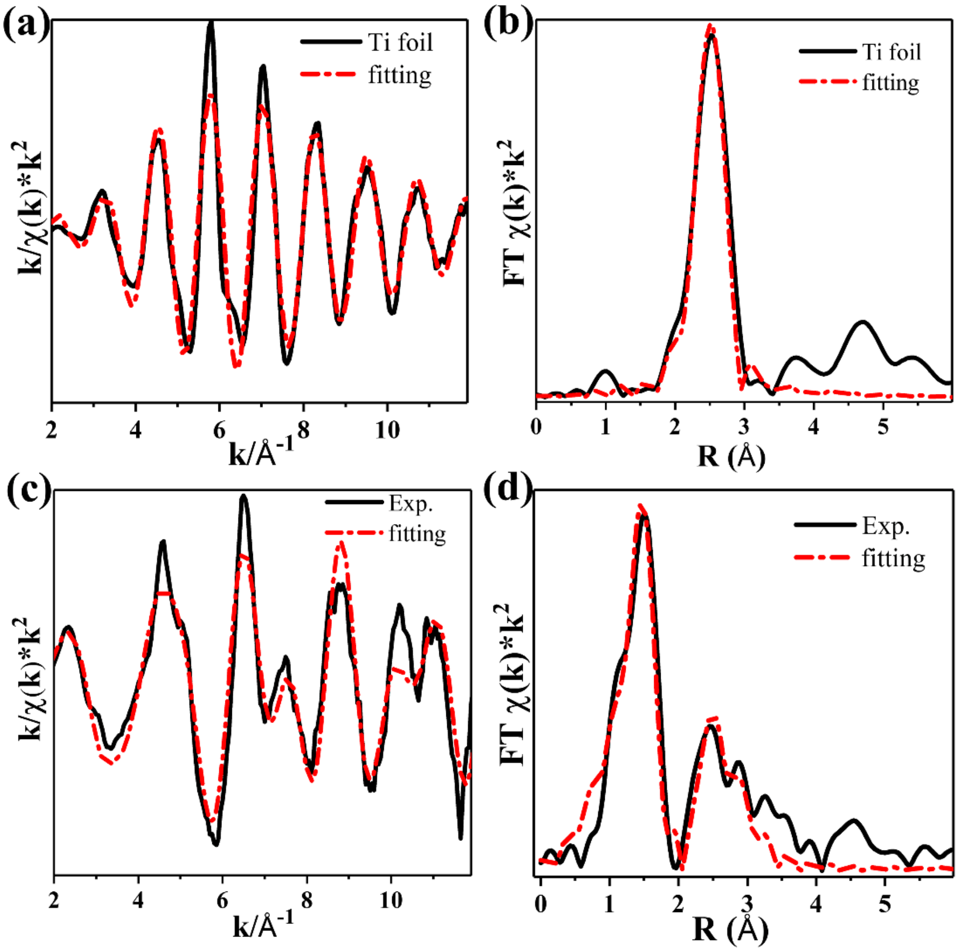

Fig. S5. Ti K edge EXAFS spectra and fitting results of (a) Ti foil k-space, (b) Ti foil R-space, (c) Au@TiO$_{2-x}$/ZnO(H300) k-space and (d) Au@TiO$_{2-x}$/ZnO(H300) R-space. The quantified fitting results are listed in Table S3.

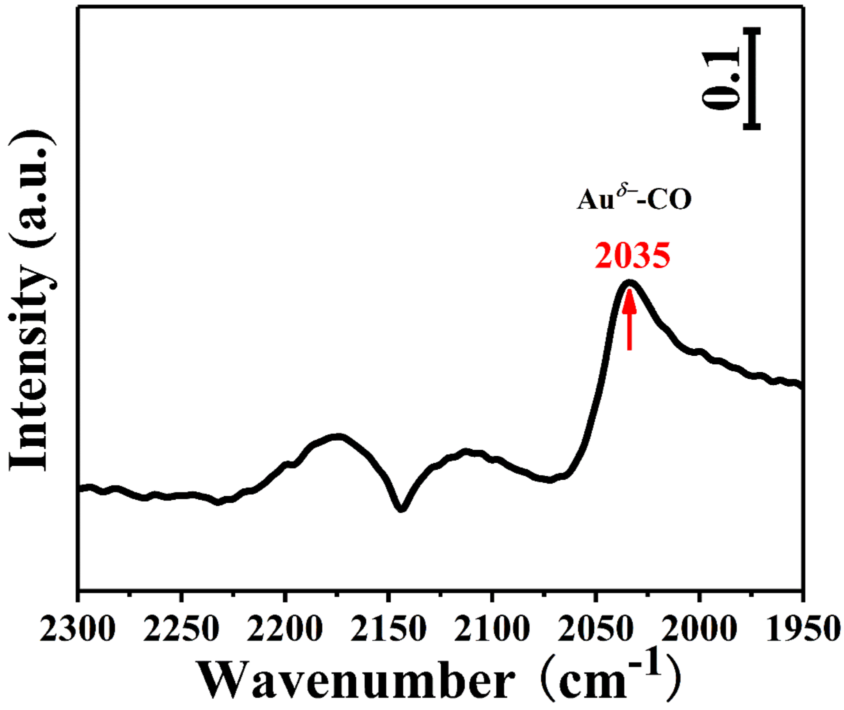

Fig. S6. *In situ* DRIFT spectra of CO adsorption on Au@TiO_{2-x}/ZnO(H300) catalyst at 200 °C.

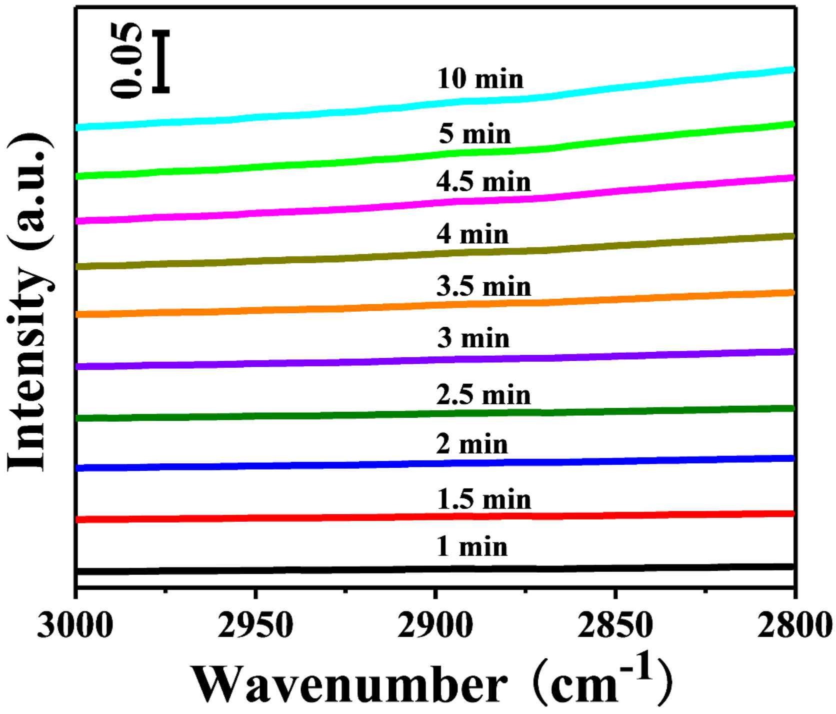

Fig. S7. *In situ* time-resolved DRIFTS spectra of CO adsorption on Au@TiO_{2-x}/ZnO(H300) catalyst recorded in 3000–2800 cm^{-1} upon exposure to H_2O atmosphere at 200 °C for prolonged time.

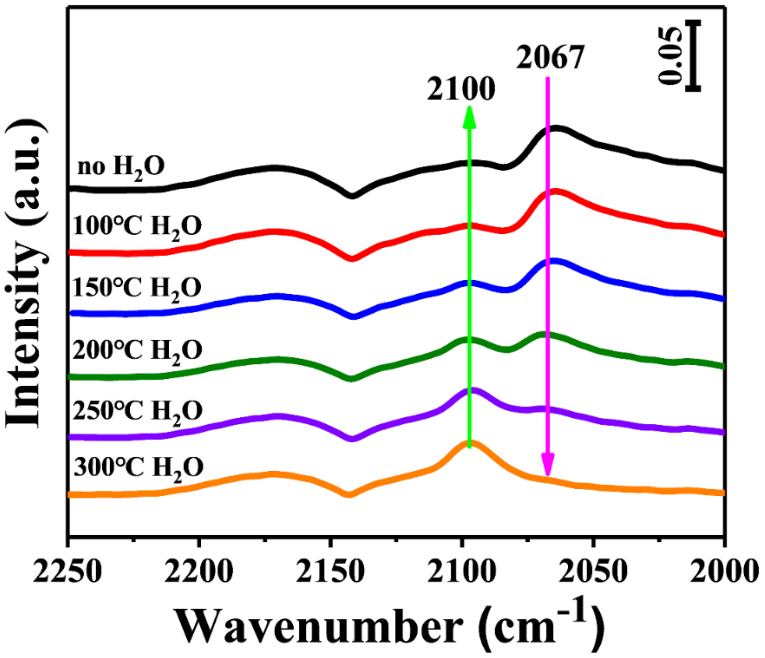

Fig. S6. *In situ* DRIFT spectra of CO adsorption on Au@TiO_{2-x}/ZnO(H300) catalyst recorded within 2250−2000 cm^{-1} after exposure to H_2O atmosphere for 10 min at various temperatures.

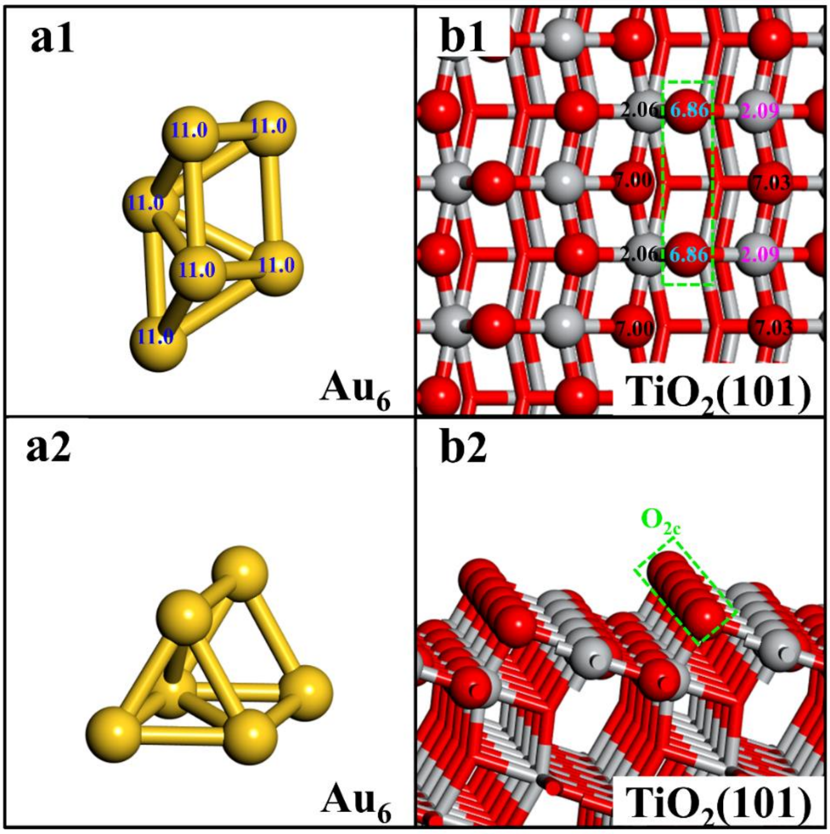

Fig. S9. Bader charge of (a) the Au_6 cluster and (b) the TiO_2 (101) slab.

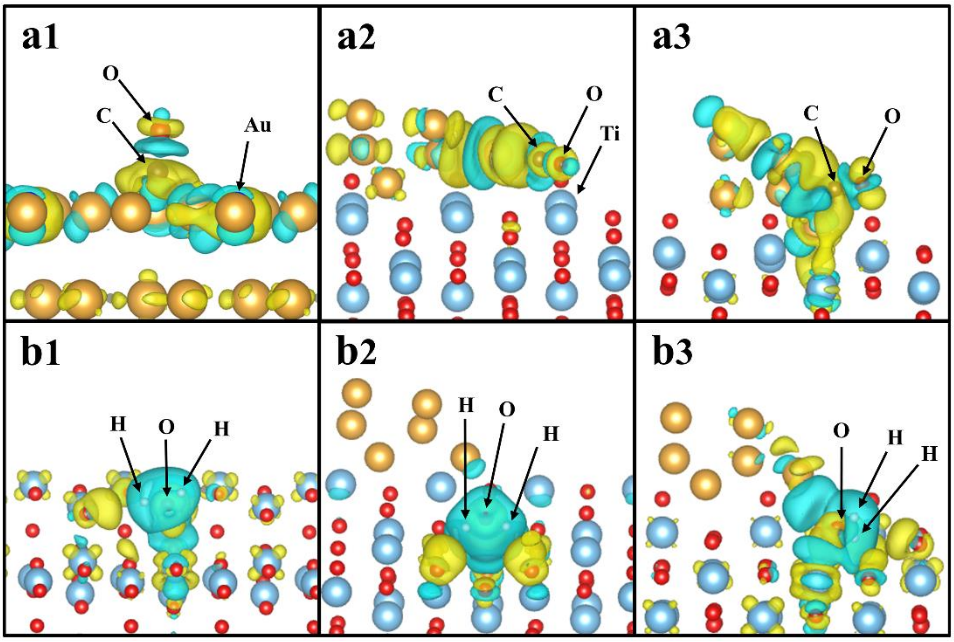

Fig. S10. Calculated electron density difference diagrams for (a) CO and (b) H_2O on various adsorption sites. Yellow represents an electron accumulation region and blue represents an electron loss region.

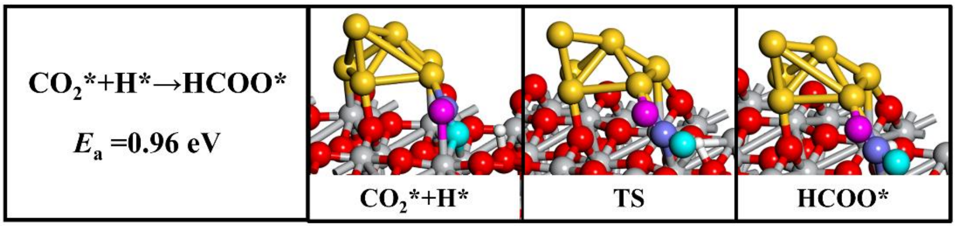

Fig. S11. Optimized structures and energy barrier for the reaction between adsorbed CO_2 and H to produce HCOO on the surface of Au/TiO_{2-x}(101).

Table S1. Activation barriers (E_a) of WGSR elementary steps on the $Au_6/TiO_{2-x}(101)$ and $Au_6/TiO_2(101)$ surface

	Elementary step	$Au_6/TiO_{2-x}(101)$	$Au_6/TiO_2(101)$
		E_a (eV)	E_a (eV)
R1	$H_2O + * \leftrightarrow H_2O*$	--	--
R2	$CO + * \leftrightarrow CO*$	--	--
R3	$H_2O* \rightarrow OH*+H*$	0.97	1.21
R4	$OH* \rightarrow O*+H*$	0.96	1.43
R5	$H*+H* \rightarrow H_2*$	0.35	1.08
R6	$CO*+O* \rightarrow CO_2*$	0.33	0.39
R7	$CO_2* \rightarrow CO_2(g)$	--	--
R8	$H_2* \rightarrow H_2(g)$	--	--

Table S2. EXAFS parameters of Au foil and Au@TiO_{2-x}/ZnO(H300) sample

Sample	Shell	CN	R (Å)	$\sigma^2/10^{-3}$Å^2	ΔE_0 (eV)
Au foil	Au–Au	12*	2.86	7.9±0.2	5.4±0.3
Au@TiO_{2-x}/ZnO(H300)	Au–O	0.4±0.1	2.06	1.0±0.6	4.9±0.6
	Au–Au	8.7±0.8	2.83		

CN, coordination number; R, bonding distance; σ^2, Debye-Waller-factor; ΔE_0, shift in absorption edge energy.

*This value was fixed during EXAFS fitting, based on the known structure of Au.

Table S3. EXAFS parameters of Ti foil and Au@TiO_{2-x}/ZnO(H300) sample

Sample	Shell	CN	R (Å)	$\sigma^2/10^{-3}$Å^2	ΔE_0 (eV)
Ti foil	Ti–Ti	6*	2.90	7.9±0.1	1.3±0.1
Au@TiO_{2-x}/ZnO(H300)	Au–O	0.4±0.1	2.06	1.0±0.6	4.9±0.6
	Ti–Au	2.1±0.6	2.74		
	Ti–Ti	1.2±0.5	3.19		

CN, coordination number; R, bonding distance; σ^2, Debye-Waller-factor; ΔE_0, shift in absorption edge energy.

*This value was fixed during EXAFS fitting, based on the known structure of Ti.

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