

## Supplementary Information

### Local Hydroxyl Groups Modified Copper Site Directs the Oxidation of Carbon Monoxide

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#### Experimental Methods

##### 1 Catalysts Preparation

Copper-Titanium dioxide (Cu-TiO<sub>2</sub>) catalysts were prepared by the precipitation method. Copper loading was designed as 10 weight% (10 wt%). 50 mL D.I. water was added into the mixture of copper (II) acetate (Sigma -Aldrich) and TiO<sub>2</sub> (Sigma-Aldrich, P25). After stirring for 10 minutes, 10 mL sodium hydroxide aqueous solution (1 M) was added to the mixture dropwise. The mixture was stirred for 1 hour before centrifugal separation. The pH value of the filtered solution was measured by a pH meter. Precipitates without further D.I. water washing are labeled as Cu-TiO<sub>2</sub>-pH14. Samples labeled as Cu-TiO<sub>2</sub>-pH9, Cu-TiO<sub>2</sub>-pH7 were synthesized with the same procedure except precipitates were further washed by D.I. water until the desired pH values were achieved. All Cu-TiO<sub>2</sub> catalysts were dried in vacuum at 50 °C overnight.

##### 2 Catalysts Characterization

###### 2.1 BET Surface Area (BET)

The Brunauer -Emmet-Teller (BET) test was performed on a Micromeritics AutoChem II 2920. Prior to the experiment, the samples were pretreated in a helium flow at 200 °C for 1.5 h and cooled to room temperature. Isotherms of N<sub>2</sub> adsorption-desorption were measured based on acquisition of N<sub>2</sub> adsorption isotherm at 77K.

###### 2.2 X-Ray Powder Diffraction (XRD)

The XRD tests were performed on a Bruker D2 Phaser desktop X-ray diffractometer equipped with a Cu X-ray source, and scans were set for a 2θ-range from 15° to 80°.

### 2.3 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were conducted on a Leeman Labs PS1000 instrument. Before each measurement, the samples were digested in an aqua regia solution (2 ml) overnight and then diluted by deionized water to obtain the desired metal concentration in a neutral pH solution.

### 2.4 Copper dispersion

Copper dispersion and the specific surface area of the metallic copper of catalyst was measured by dissociative N<sub>2</sub>O oxidation and H<sub>2</sub> titration. Typically, 25 mg catalysts were first pretreated in a helium flow at 200 °C for 1.5 h and cooled to room temperature to remove moisture and impurities that may remain on the surface. Then catalysts were reduced in a 10 % H<sub>2</sub>/Ar mixture at a flow rate of 30 mL/min from room temperature to 200 °C. The hydrogen consumption from this reduction process was assigned as A<sub>1</sub>. Pure He (30 mL/min) was purged into the reactor to the samples to 50 °C. The catalyst was oxidized by 10 % N<sub>2</sub>O/He (30 mL/min) at 60 °C for 0.5 h. Subsequently, pure He (30 mL/min) flowed through the sample for 0.5 h to remove the residual N<sub>2</sub>O. Finally, another reduction process was performed in 10 % H<sub>2</sub>/Ar (30 mL/min). Hydrogen consumption from the second reduction process was denoted as A<sub>2</sub>. The dispersion of Cu (D<sub>Cu</sub>, %) was calculated as follows

$$D = \frac{2A_2}{A_1} \times 100\%$$

### 2.5 In-situ Diffuse Reflectance Fourier Transform Infrared Spectroscopy (in-situ DRIFTS)

In-situ diffuse reflectance Fourier transform infrared spectroscopy (in-situ DRIFTS) experiments were performed using a Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with a MCT detector and a KBr beam splitter. Samples were first pre-treated with pure helium at 200 °C for 1.5 hrs, before the gas mixture (1%CO, 20%O<sub>2</sub> balanced in Helium) was introduced. All the background scans of the samples were collected under helium prior to the reaction.

### 2.6 Temperature Programmed Reactions

Hydrogen Temperature Programmed Reduction (H<sub>2</sub>-TPR) was conducted on Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector. In a typical H<sub>2</sub>-TPR experiment, 50 mg of sample were pretreated with pure helium at 200 °C for 1.5 h to remove moisture and impurities on the surface. The reduction profiles were collected from room temperature to certain temperature with the heating rate as 5 °C/min while 10 % H<sub>2</sub>/Ar gas mixture (30 mL/min) flowing through samples. The hydrogen consumption calculation was based on calibrations using Ag<sub>2</sub>O standard sample under the same test conditions.

Carbon monoxide Temperature Programmed Surface Reaction (CO-TPSR) was performed in a home-made fixed bed flow reactor. 50 mg of catalyst was loaded in a quartz reactor (I.D. = 10 mm). Prior to the experiment, same pretreatment underwent the same procedure in H<sub>2</sub>-TPR. The profiles were collected

with the heating rate as 5 °C/min while 10%CO/Helium gas mixture (30 mL/min) flowing through the samples. The CO signal was monitored using an MKS e-Vision 2 residual gas analyzer (RGA).

### 2.7 X-ray Photoelectron Spectroscopy (XPS)

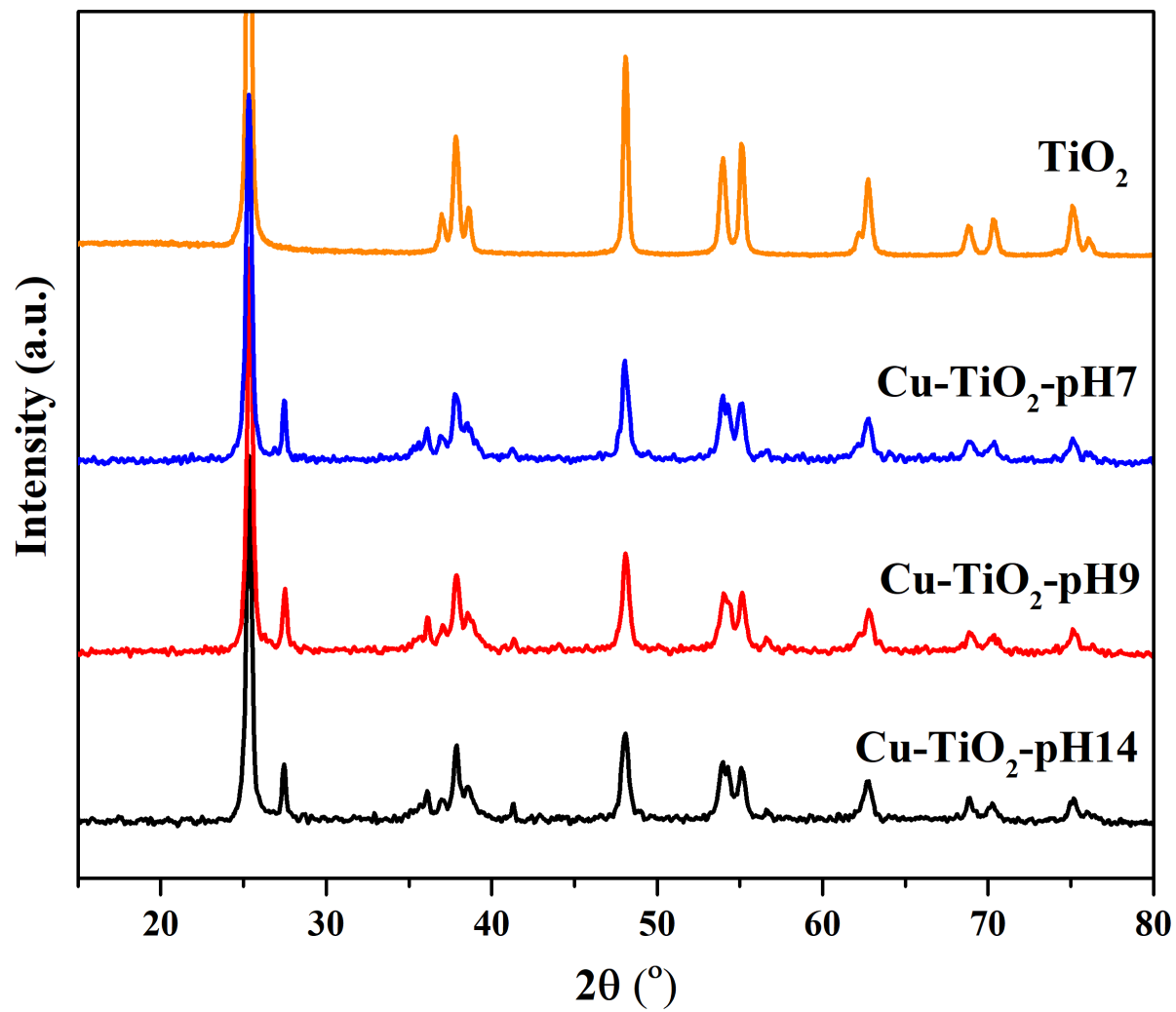
X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific K-Alpha system equipped with an Al source and a 180° double focusing hemispherical analyzer with a 128- channel detector at a pass energy of 50 eV for the analyses of the core level signals of Cu 2p, Ti 2p and O 1s. When processing the XPS spectra data, binding energy values were referenced to C 1s peak (284.8 eV) to eliminate the effect of surface adventitious contamination layer to correct the shift caused by charge effect.

### 3 Activity test

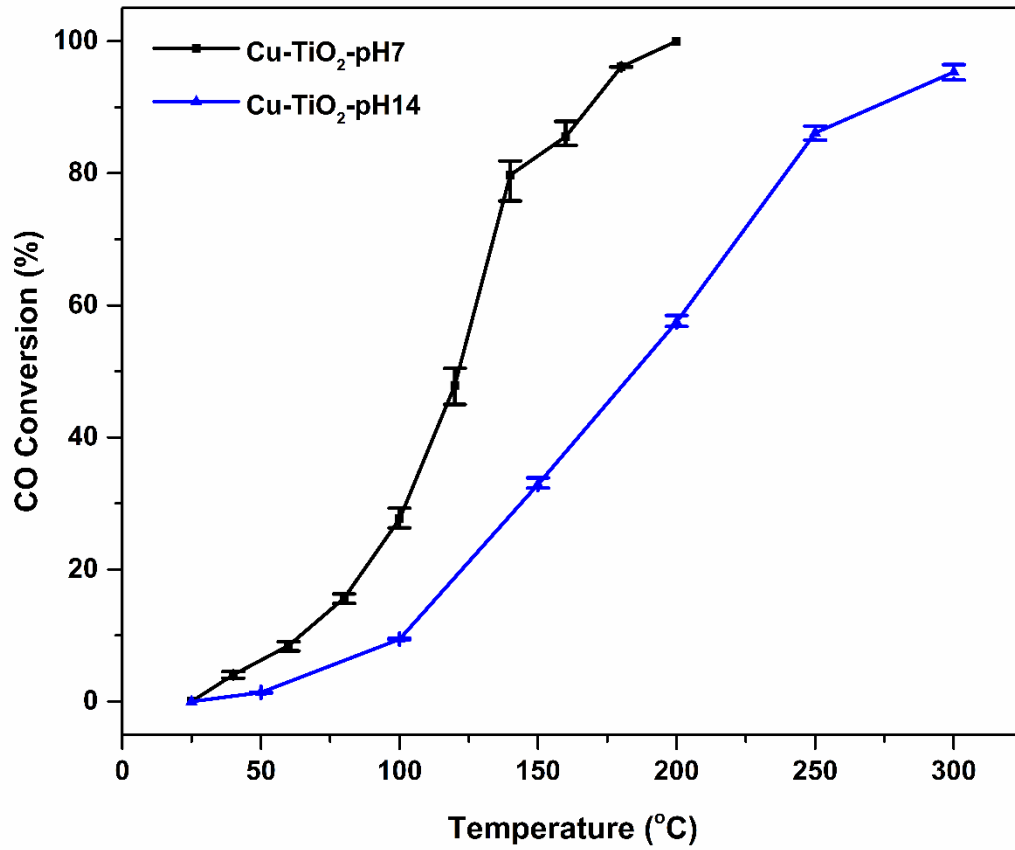
The carbon monoxide oxidation reaction light-off test was performed in a fixed bed flow reactor equipped with a temperature controller. Typically, 50 mg of catalyst was filled in a quartz tube (I. D. = 10 mm). The reaction temperature was measured with a K-type thermocouple reaching the top of the catalyst bed. The samples were pre-treated with pure helium at 200 °C for 1.5 h before being passed through the reaction gas stream. The flow rate was 30 mL/min, and heating rate was 5 °C/min. Reactant gas (1% CO, 20% O<sub>2</sub> balanced with helium) was used for activity tests. The gas flow was also 30 mL/min, which gave the gas hourly space velocity "GHSV" as 36,000 mL·h<sup>-1</sup>·g<sup>-1</sup>. The CO and CO<sub>2</sub> concentration from outlet stream were analysed online using a Gas Chromatograph (SRI 8160C).

The stability test was performed following the same procedure of the light-off test. After the first trial of the light-off test, pure helium was introduced to replace reactant gases in the reaction system. Then samples were cooled down to room temperature under pure helium before starting the next light-off test. The same procedure was also repeated for the third trial.

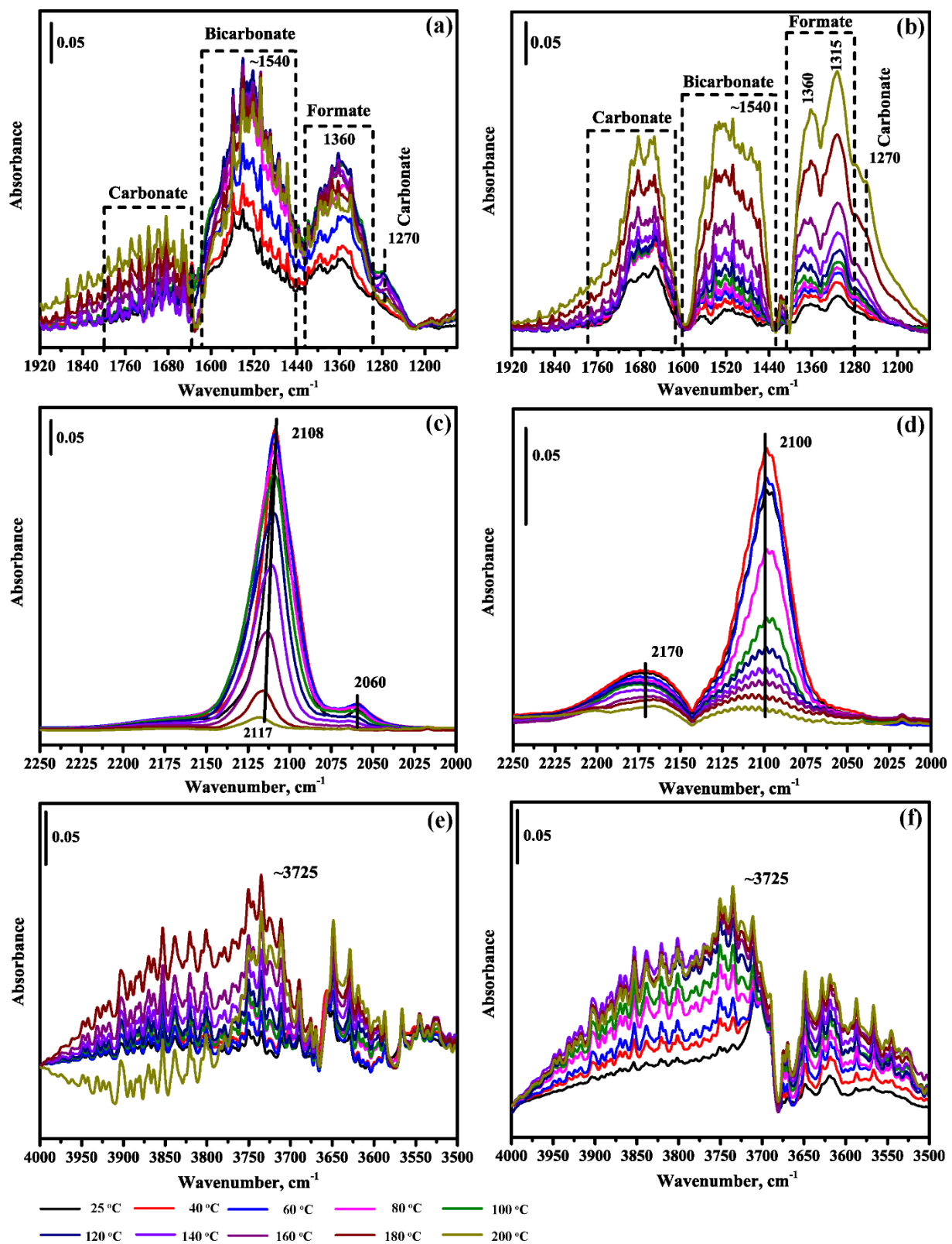
Supporting Figures



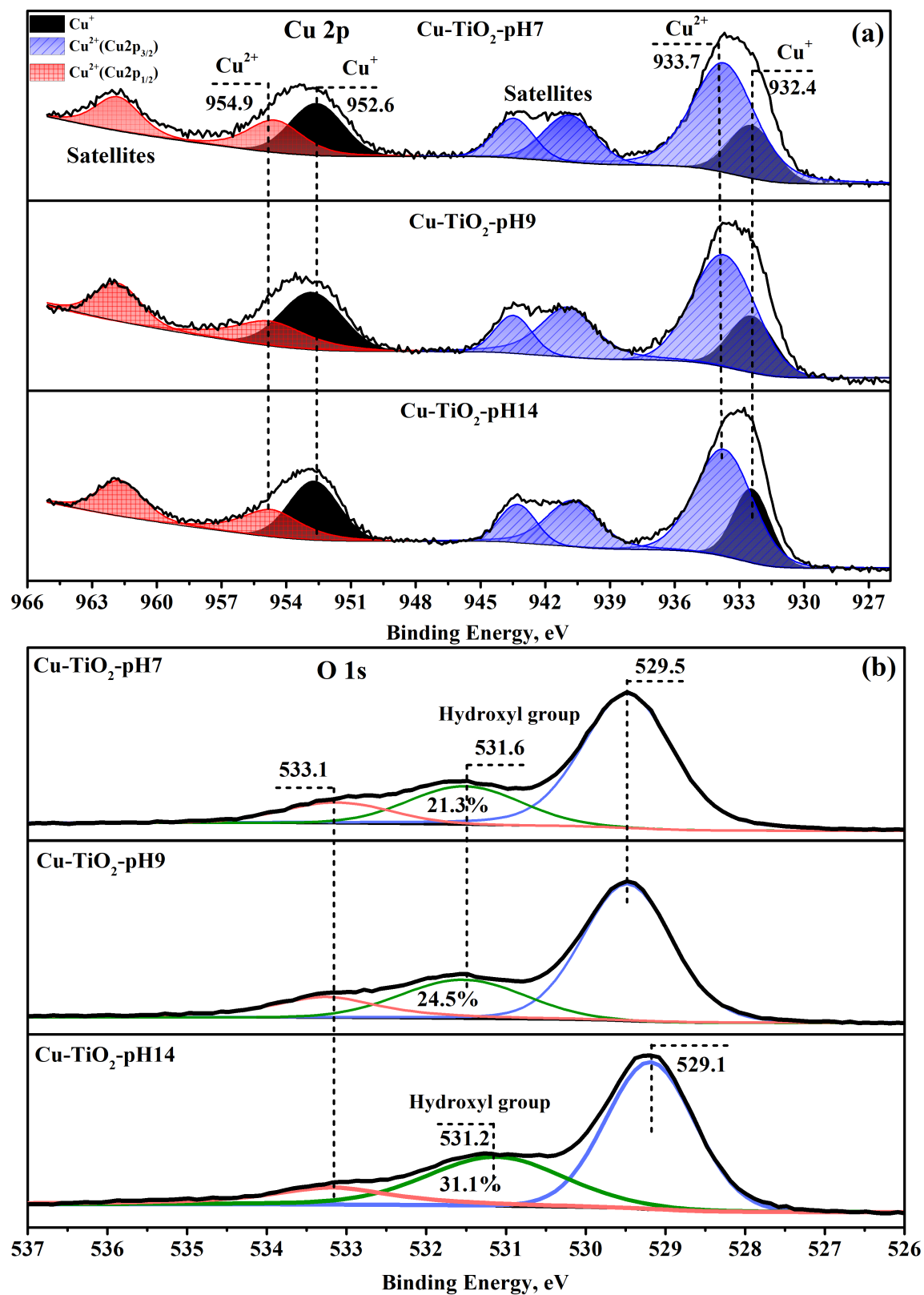
**Figure S1** X-Ray Diffraction (XRD) patterns of TiO<sub>2</sub> and Cu-TiO<sub>2</sub> catalysts.



**Figure S2** Cyclic light-off curves of Cu-TiO<sub>2</sub>-pH7 and Cu-TiO<sub>2</sub>-pH14 in CO oxidation reaction. Error bar indicates the difference among three trials.



**Figure S3** In-situ DRIFTS profiles over the Cu-TiO<sub>2</sub>-pH7 catalyst (a, c, e) and the Cu-TiO<sub>2</sub>-pH14 catalyst (b, d, f).



**Figure S4** XPS profiles of (a) Cu 2p and (b) O 1s over Cu-TiO<sub>2</sub> catalysts.

- The existence of  $\text{Cu}^{2+}$  is confirmed by the typical  $\text{Cu } 2p_{3/2}$  peak located at 933.7 eV and two intense shake-up satellites in the range of 938–945 eV. The  $\text{Cu } 2p_{1/2}$  peak located at 954.9 eV and its shake-up satellites identified at 960–965 eV can also be attributed to  $\text{Cu}^{2+}$ .
- The peak located at 932.4 eV is assigned to  $\text{Cu}^+$ .
- The weak peak located at 533.1 eV is assigned to the oxygen bonds of the chemisorbed  $\text{H}_2\text{O}$ . Meanwhile, the peak at 531.6 eV is attributed to surface hydroxyl groups.