# Supplementary Information

# Nitrogen Modified Titanium Dioxide (N-TiO$_2$) Promotes Carbon Monoxide Oxidation over Copper Catalysts

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## 1. Catalysts Preparation

*Nitrogen modified TiO₂* (*N-TiO₂*) Typically titanium dioxide (P25, Sigma-Aldrich) and urea (Sigma-Aldrich) were physically mixed with mass ratio of $TiO_2$ and urea as 1:5. The mixture was placed in vacuum oven under room temperature overnight. The dried mixtures were calcined at 550 $^{\circ}$C for 15 hours. Calcined samples were symbolized as *N-TiO₂*.

*Cu-N-TiO₂* Copper (II) acetate (Sigma-Aldrich) and N-TiO₂ supports were mixed with D.I. water and stirred for 5 minutes. 10 mL sodium hydroxide solution (1M) was added dropwise to the mixture. After 1 hour stirring at room temperature, the precipitate was separated through centrifuge, followed by D. I. water washing until the pH value of the washing solution reaches 7. The as-prepared samples were dried at 50 $^{\circ}$C under vacuum. The copper weight was designed as 10 weight%. Dried samples were symbolized as *Cu-N-TiO₂*.

*Cu-TiO₂* The same procedure as Cu-N-TiO₂ was applied to synthesize Cu-TiO₂. TiO₂ (P25, Sigma-Aldrich) were calcined at 550 $^{\circ}$C for 15 hours before introducing copper.

## 2. Characterization

### BET Surface Area

The Brunauer-Emmet-Teller (BET) test was performed on Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector. Prior to the test, samples were pre-treated with pure helium at 200 °C for1.5 h. Isotherms of $N_2$ adsorption -desorption were measured based on acquisition of $N_2$ adsorption isotherm at 77K.

### Raman Spectroscopy

Raman spectra was collected with a NT-MDT Raman spectrometer using diode laser beam. An excitation wavelength of 532 nm was used. Spectrum were collected by co-adding five scans of 10 s and the laser power of $22 \pm 2$ mW under ambient conditions.

### 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 pretreated with pure helium at 200 °C for 1.5 hrs. A gas mixture (1%CO, 20%O₂ balanced in Helium) was introduced. The tested were conducted at 80 $^{\circ}$C, 100 $^{\circ}$C, 120 $^{\circ}$C,

140 ºC, 160 ºC and 180 ºC. All the background scans of the samples were collected under helium prior to the reaction.

**Surface Copper Dispersion**

Copper dispersion and the specific surface area of metallic copper of catalyst was measured by dissociative $N_2O$ oxidation and $H_2$ 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% $H_2$/Ar mixture at a flow rate of 30 mL·min$^{-1}$ from room temperature to 200 ºC. The hydrogen consumption from this reduction process was assigned as $A_1$. Pure He (30 mL·min$^{-1}$) was purged into reactor to the samples to 50 ºC. The catalyst was oxidized by 10% $N_2O$/He (30 mL·min$^{-1}$) at 60 ºC for 0.5 h. Subsequently, pure He (30 mL·min$^{-1}$) flowed through the sample for 0.5 h to remove the residual $N_2O$. Finally, another reduction process was performed in 10% $H_2$/Ar (30 mL·min$^{-1}$). Hydrogen consumption from the second reduction process was denoted as $A_2$. The dispersion of Cu (D, %) was calculated as follows:

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

The specific surface area of metallic copper (S, m$^2$·g$^{-1}$) was calculated by

$$S = 2 \times A_2 \times N_A/(A_1 \times M_{Cu} \times 1.4 \times 10^{19}) = 1353 \times \frac{A_2}{A_1}$$

where $N_A$ is Avogadro's constant, $M_{Cu}$ is the relative atomic mass of copper (63.46 g/mol), and $1.4 \times 10^{19}$ is the number of copper atom of per square meter when the average surface area of copper atom is assigned as $7.11 \times 10^{-2}$ nm$^2$.

**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, N 1s, 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.

**Temperature Programmed Reactions**

Hydrogen-Temperature Programmed Reduction ($H_2$-TPR) was conducted on Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector. In a typical H2-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$^{-1}$ while 10% H$_2$/Ar mixture (30 mL·min$^{-1}$) flowing through samples. The hydrogen consumption calculation was based on calibrations using Ag$_2$O standard sample under the same test conditions.

O$_2$-Temperature Programmed Reaction (O$_2$-TPR) followed the same procedure as H$_2$-TPR, except the carrier gas was 10%O$_2$/Helium.

**Catalytic Activity Test**

The carbon monoxide oxidation reaction was performed in a home-made fixed bed flow reactor. Typically, 50 mg of catalyst was loaded in quartz tube (O.D. = 10 mm). The reactant gas (1% CO, 20%O$_2$ balanced with He) flows through the catalyst bed with the flow rate of 30 ml·min$^{-1}$. The samples were pre-treated with pure helium at 200 °C for 1.5 h before activity tests. The concentrations of carbon monoxide and carbon dioxide were analysed with a gas chromatograph (SRI 8160C).

**Table S1.** Analysis of Hydrogen-Temperature Programmed Reduction (H$_2$-TPR) Profiles

| Sample | Peak I | | Peak II | | Peak III | | Peak IV | |
|---|---|---|---|---|---|---|---|---|
| | T(°C) | H$_2$ Consumption $\mu mol$·gcatal$^{-1}$ (%) | T(°C) | H$_2$ Consumption $\mu mol$·gcatal$^{-1}$ (%) | T(°C) | H$_2$ Consumption $\mu mol$·gcatal$^{-1}$ (%) | T(°C) | H$_2$ Consumption $\mu mol$·gcatal$^{-1}$ (%) |
| Cu-N-TiO$_2$ | 76 | 186.0 (12.4%) | 90 | 431.1 (28.8%) | 115 | 735.4 (49.2) | 132 | 142.1 (9.6%) |
| Cu-TiO$_2$ | | | 93 | 270.2 (18.8%) | 120 | 829.4 (57.8) | 136 | 334.6 (23.4%) |

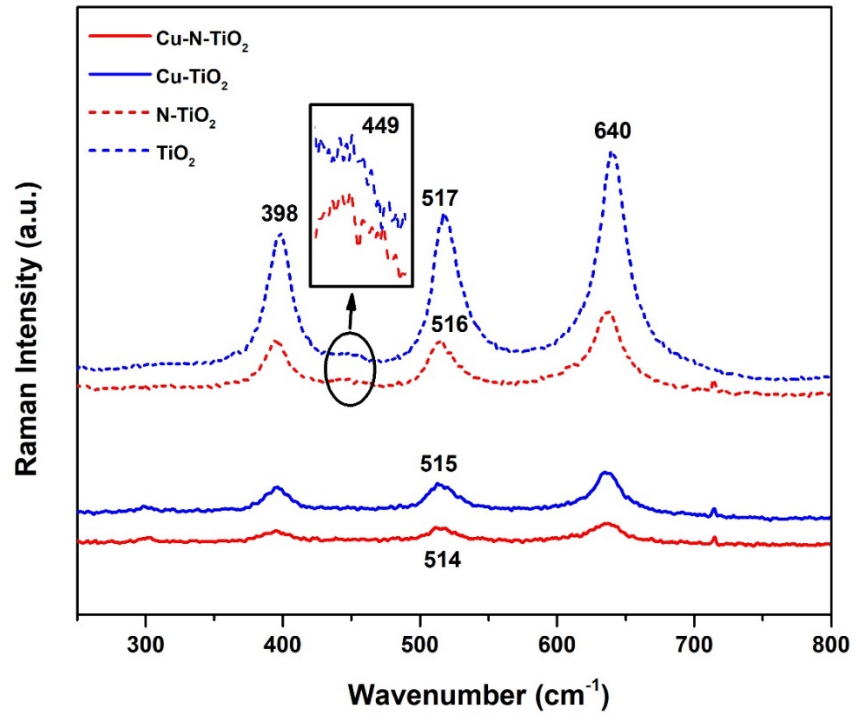**Fig. S1** Raman spectra of supports and copper modified catalysts.

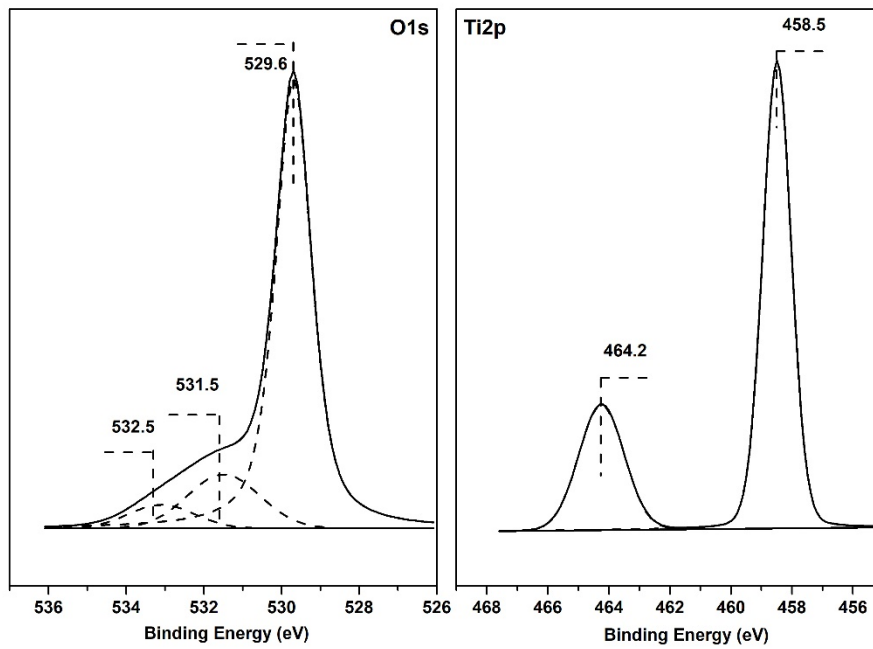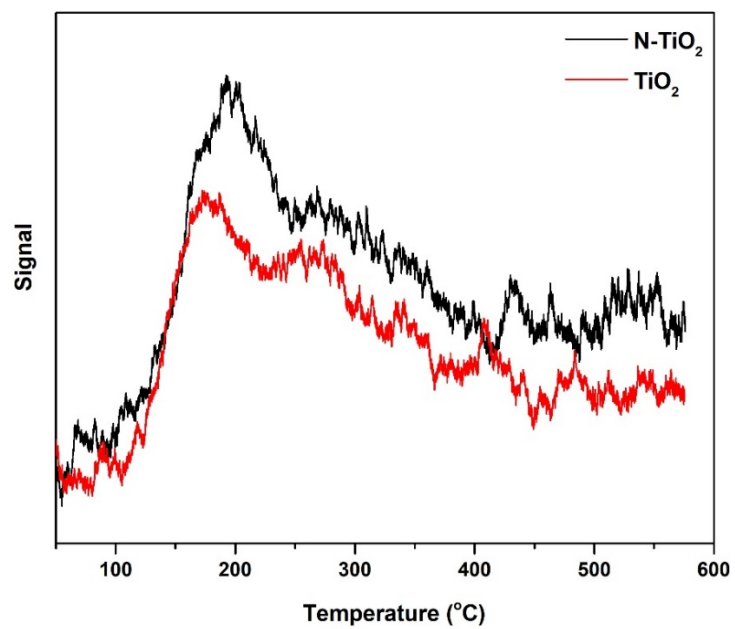**Fig. S2** XPS spectra of *O1s* and *Ti 2p* for TiO$_2$ catalyst.

**Fig. S3** $O_2$-Temperature Programmed Reaction ($O_2$-TPR) profiles of N-TiO$_2$ and TiO$_2$ supports.
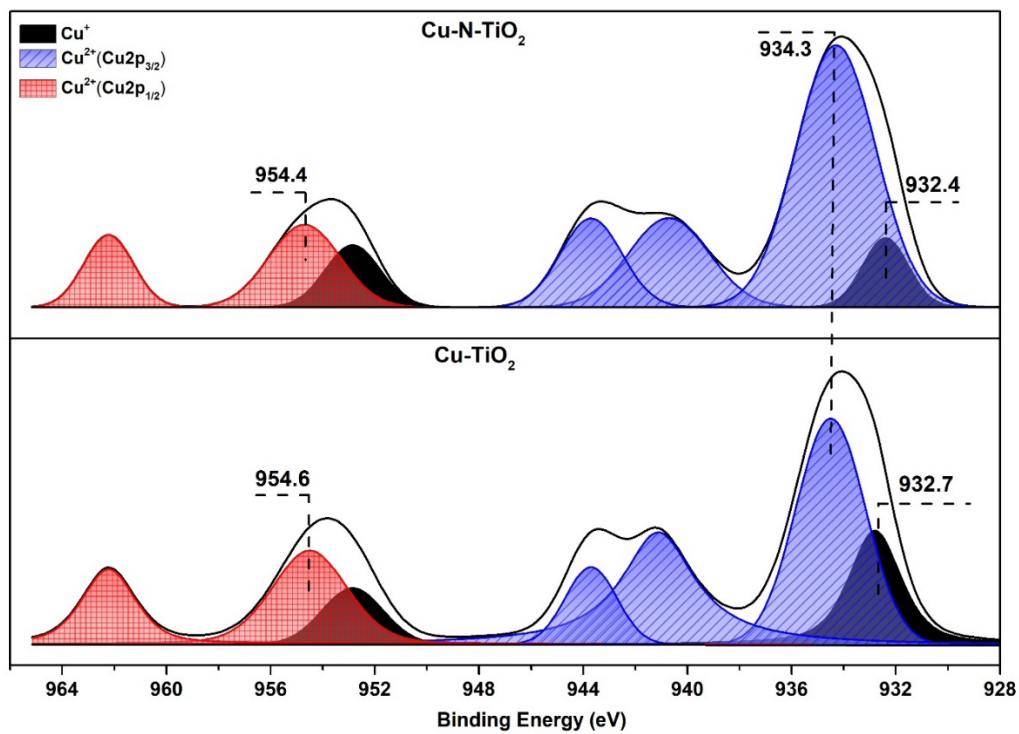
**Fig. S4** XPS spectra of *Cu 2p* for Cu-TiO$_2$ and Cu-N-TiO$_2$ catalysts.