

## Supporting Information

# **Cu and Si co-doping on TiO<sub>2</sub> nanosheets to modulate reactive oxygen species for efficient photocatalytic methane conversion**

Jun Ma,<sup>a,b</sup> Jingxiang Low,<sup>a</sup> Di Wu,<sup>a</sup> Wanbing Gong,<sup>a</sup> Hengjie Liu,<sup>a</sup> Dong Liu,<sup>\*a,b</sup> Ran Long,<sup>\*a</sup> and Yujie Xiong,<sup>\*a</sup>

<sup>a</sup> Hefei National Research Center for Physical Sciences at the Microscale, School of Chemistry and Materials Science, National Synchrotron Radiation Laboratory, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China.

<sup>b</sup> Suzhou Institute for Advanced Research, University of Science and Technology of China, Suzhou, Jiangsu 215123, China.

E-mail: dongliu@ustc.edu.cn, longran@ustc.edu.cn and yjxiong@ustc.edu.cn

## Method

### Synthesis of Cu and Si co-doped ultrathin TiO<sub>2</sub> nanosheets

Typically, 2.5 mL of tetrabutyl titanate was dissolved in 10 mL anhydrous ethanol under stirring, and then specific amounts of Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O (17.8 mg) and tetraethyl orthosilicate (e.g., 100 μL) were added. Subsequently, 0.3 mL hydrofluoric acid (HF, 40 wt.%) was added into the solution. After stirring for 0.5 h, the solution was transferred into a Teflon-lined autoclave (20 mL) and heated at 180 °C for 2 h. After cooling down to room temperature, the TiO<sub>2</sub> nanosheets were collected by centrifugation and washed with ultrapure water for three times. Finally, the as-prepared TiO<sub>2</sub> nanosheets were dried at 80 °C for 24 h.

### Sample characterizations

Transmission electron microscopy (TEM) images were taken on a Hitachi Model H7700 microscope at 100 kV. High-resolution TEM (HRTEM) images, the scanning TEM (STEM) image, and energy-dispersive X-ray spectroscopy (EDS) mapping profiles were recorded on an FEI Talos F200X field-emission high-resolution transmission electron microscope at 200 kV.

X-ray photoelectron spectroscopy (XPS) was conducted on PHI 5000 VersaProbe III using a monochromatic Al Kα X-ray source under the high power mode.

Powder X-ray diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super X-ray diffractometer with Cu-Kα radiation ( $\lambda = 1.54178 \text{ \AA}$ ).

UV–vis–NIR diffuse reflectance spectra were recorded in the spectral region of 250–1200 nm with a Shimadzu SolidSpec-3700 spectrophotometer.

EPR spectra were collected using a JEOL JES-FA200 electron spin resonance spectrometer at room temperature (9.062 GHz).

### Detection of hydroxyl radical (•OH)

5, 5-dimethyl-1-pyrroline N-oxide (DMPO) was used to trap the generated hydroxyl radical in the reaction system. Briefly, the TiO<sub>2</sub> nanosheets and DMPO were dispersed in ice-cold ultrapure water, respectively. The solution containing TiO<sub>2</sub> nanosheets was vigorously shaken for 10 s after the addition of DMPO solution. The mixture was irradiated using a 300 W Xe lamp for 30 s, and then was analyzed by EPR spectroscopy.

### Photoelectrochemical measurements

All photoelectrochemical measurements were performed in a three-electrode system

using electrochemical workstation (CHI 760E, Shanghai Chenhua, China). A 300 W Xe lamp (Beijing Perfectlight PLS-SXE300D) with a power density of  $100 \text{ mW cm}^{-2}$  was used as light source during the photoelectrochemical measurements. The prepared samples dropped on FTO glass were used as photoelectrode, a Pt foil as counter electrode, and a Ag/AgCl electrode as reference electrode. The three electrodes were inserted in a quartz cell which was prefilled with 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte (pH = 6.6) and purged with Ar for 30 min before the measurements.

### **Mott–Schottky plots measurement**

Mott–Schottky plots were recorded in 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte (pH = 6.6) at a frequency of 1 kHz. Charge carrier density was calculated from the slope of Mott–Schottky plots according to the equation:

$$1/C^2 = (2 / q\epsilon\epsilon_0N_d) (E - E_{fb} + k_B T/q) \quad (2)$$

where  $\epsilon$  is the dielectric constant of  $\text{TiO}_2$ ,  $\epsilon_0$  is the permittivity of vacuum,  $C$  is the interfacial capacitance,  $N_d$  is the number of donors and acceptors,  $E$  is the applied voltage,  $E_{fb}$  is the flat-band potential,  $k_B$  is the Boltzmann's constant,  $T$  is the absolute temperature, and  $q$  is the electronic charge.

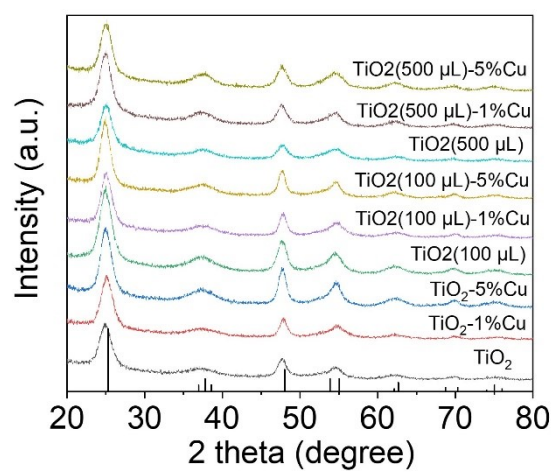
### ***In situ* DRIFTS characterization**

*In situ* DRIFTS measurements were performed using a Bruker IFS 66v Fourier-transform spectrometer equipped with a Harrick diffuse reflectance accessory at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) of NSRL. Each spectrum was recorded by averaging 256 scans at a resolution of  $4 \text{ cm}^{-1}$ . The samples were placed in an infrared (IR) reaction chamber sealed with ZnSe windows, which is specifically designed to examine highly scattered powder samples in diffuse reflection mode. After sample loading, the chamber was purged with argon gas (99.999%) for 30 min. Then the spectrum was collected as background spectrum. During the *in situ* characterization, pure  $\text{CH}_4$  gas (99.999%) was continually introduced into the chamber.

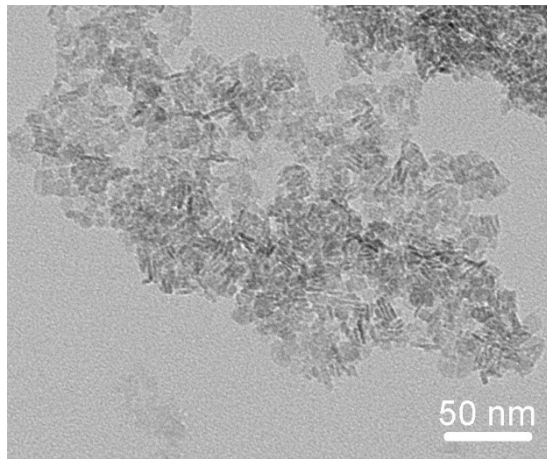
### **Photocatalytic methane conversion measurements**

5 mg of the prepared  $\text{TiO}_2$  nanosheets were put into a hermetic quartz tube contained 5 mL ultrapure water. The device was purged with  $\text{CH}_4$  flow for 20 min to eliminate the air prior to photocatalysis, and was then illuminated with 300 W Xe lamp (Perfect Light PLS-SXE300D) at a specific power density (e.g.,  $200 \text{ mW cm}^{-2}$ ) for 4 h. The products were detected by gas chromatography (GC, 7890B, Ar carrier, Agilent) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). Each value of production rate was measured for three times to ensure the accuracy of the photocatalytic results.

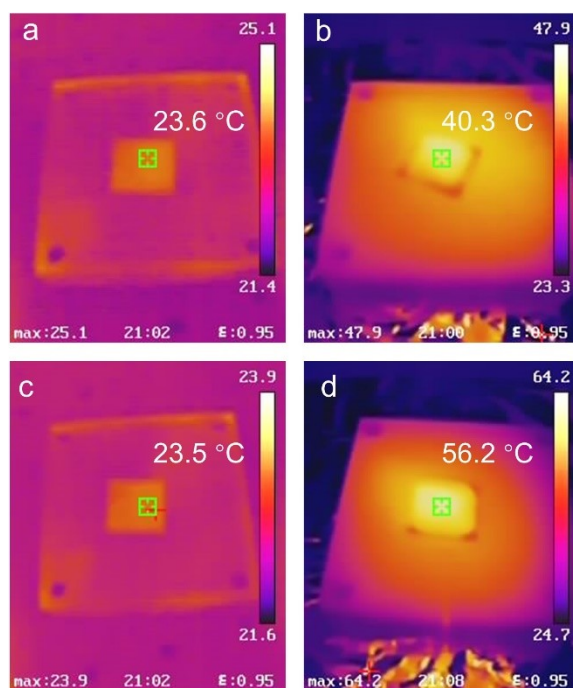




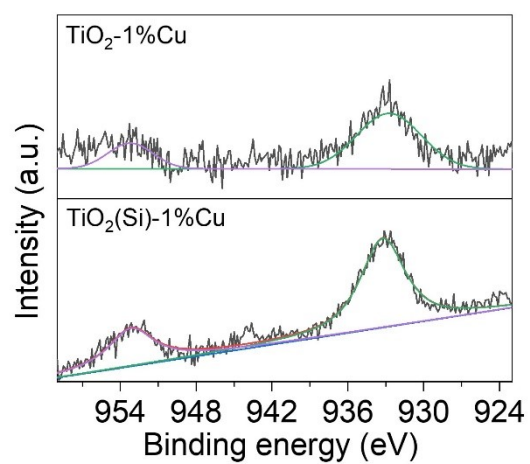
**Figure S1.** XRD patterns of prepared Cu and Si co-doped ultrathin TiO<sub>2</sub> nanosheets.



**Figure S2.** TEM images of the prepared TiO<sub>2</sub> nanosheets.

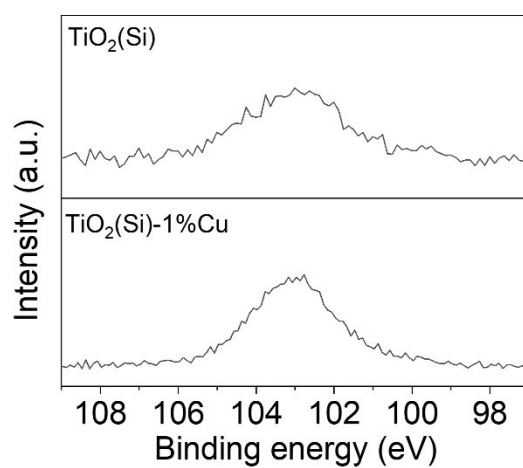


**Figure S3.** The thermography images of  $\text{TiO}_2$  (a) in the dark and (b) under Xenon lamp irradiation ( $200\text{ mW cm}^{-2}$ ). The thermography images of  $\text{TiO}_2(\text{Si})\text{-1\%Cu}$  (a) in the dark and (b) under Xenon lamp irradiation ( $200\text{ mW cm}^{-2}$ ).

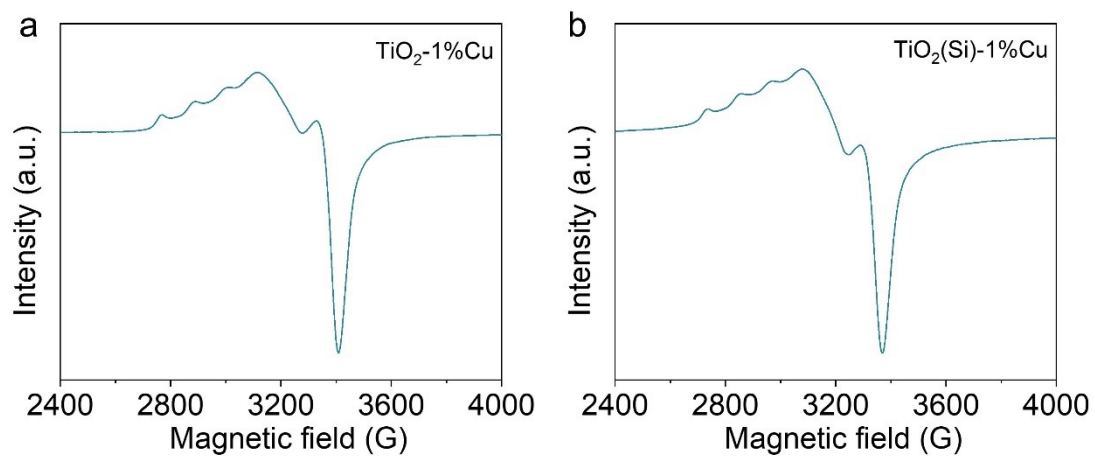


**Figure S4.** The refined Cu 2p XPS spectra of  $\text{TiO}_2\text{-1\%Cu}$  and  $\text{TiO}_2(\text{Si})\text{-1\%Cu}$ .

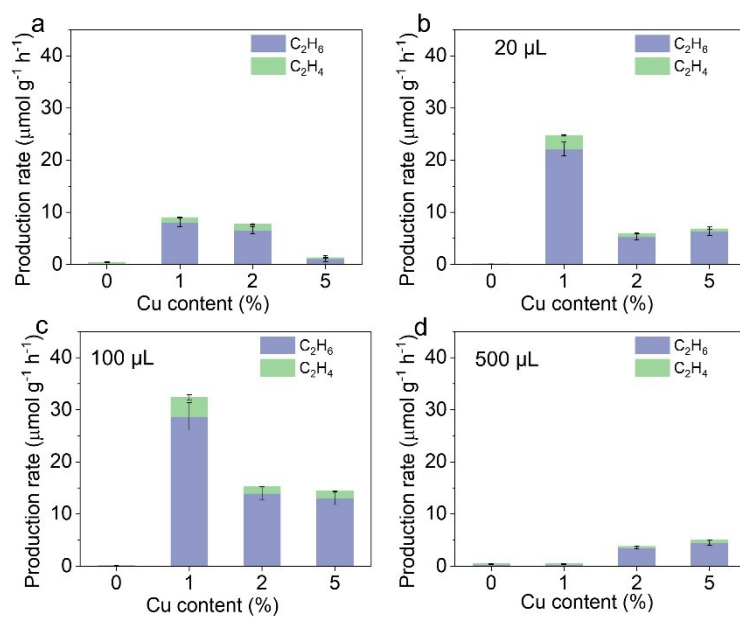




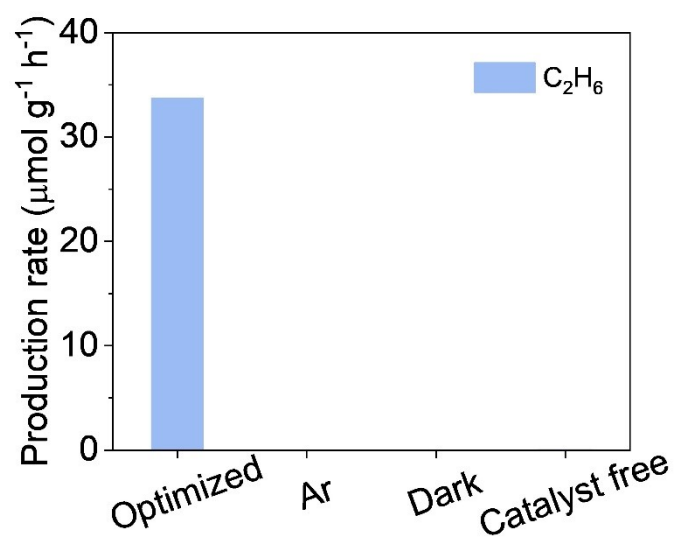
**Figure S5.** The Si 2p spectra of  $\text{TiO}_2(\text{Si})$  and  $\text{TiO}_2(\text{Si})\text{-1\%Cu}$ .



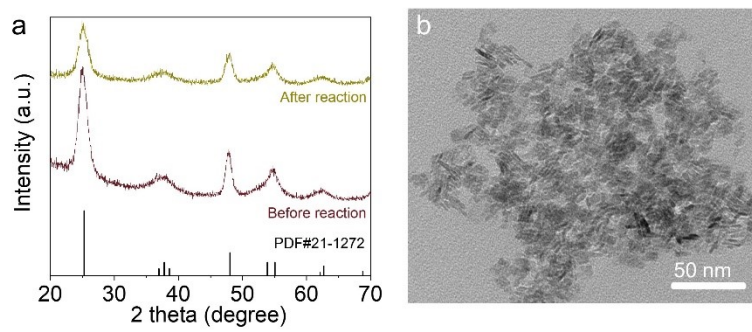
**Figure S6.** The EPR spectra for  $\text{TiO}_2\text{-1\%Cu}$  and  $\text{TiO}_2(\text{Si})\text{-1\%Cu}$ .



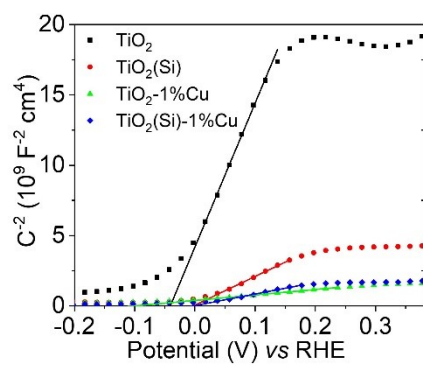
**Figure S7.** Photocatalytic performance of the prepared TiO<sub>2</sub> nanosheets after 4 h of light irradiation.



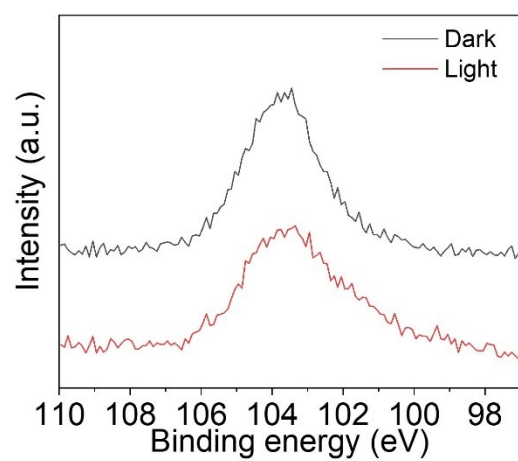
**Figure S8.** The ethane production from the control experiments in the absence of methane, light irradiation or photocatalyst.



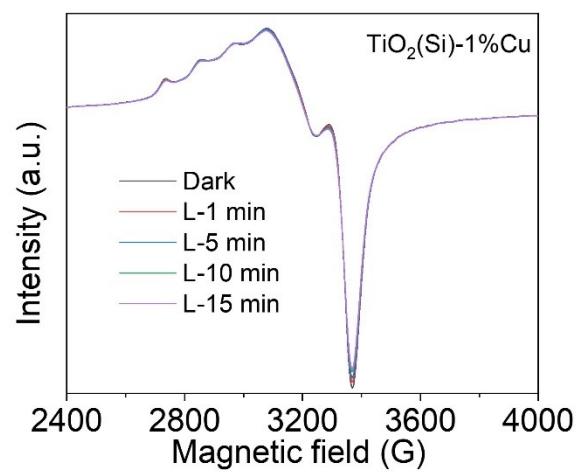
**Figure S9.** The XRD patterns and TEM image of TiO<sub>2</sub>(Si)-1%Cu after photocatalytic methane conversion.



**Figure S10.** The Mott-Schottky plot for different  $TiO_2$  samples collected at a frequency of 1 kHz.

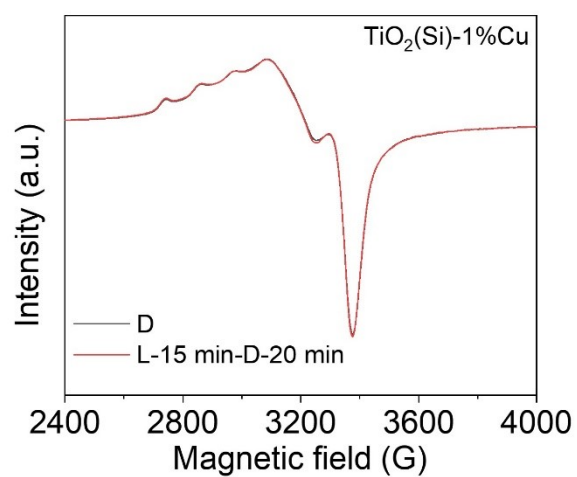


**Figure S11.** The light irradiated Si 2p XPS spectra for TiO<sub>2</sub>(Si)-1%Cu.

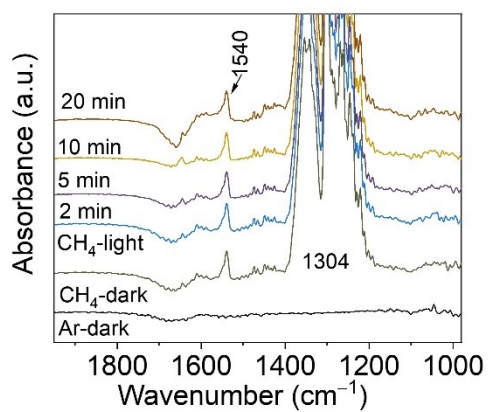


**Figure S12.** The EPR spectra for  $\text{TiO}_2(\text{Si})-1\% \text{Cu}$  in dark and irradiated for different time.





**Figure S13.** The EPR spectra for the pristine  $\text{TiO}_2(\text{Si})\text{-1\%Cu}$  and the irradiated  $\text{TiO}_2(\text{Si})\text{-1\%Cu}$  after exposed in air for 20 min.



**Figure S14.** *In situ* DRIFTS spectra for photocatalytic methane conversion over TiO<sub>2</sub> nanosheets under light irradiation.