

## Supporting Information

### Room-temperature Coupling of Methane with Singlet Oxygen

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## **Materials and methods**

### **Chemicals**

Degussa P25 nanopowder (21nm, Macklin) was used as catalyst. Oxone (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>) was dissolved in deionized water to form a solution of peroxymonosulfate (HSO<sub>5</sub><sup>-</sup>) (1 mol/L). Potassium bichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), benzoquinone (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>), ethanol, tert-butanol (TBA), furfuryl alcohol (11.33 mol/L) were used in trapping experiments. All above chemicals were analytical grade purity. H<sub>2</sub>O<sub>2</sub> (30%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Ultrahigh purity CH<sub>4</sub> (>99.999%), N<sub>2</sub> (99.999%) were supplied by Air Liquide. CO<sub>2</sub> (99.999%), O<sub>2</sub> (99.999%) were supplied by Shanghai Weichuang Standard Gas Analytical Technology Co., Ltd.

### **Characterization**

The crystalline phase was identified via X-ray diffraction (XRD, SHIMAZDU XRD-6100) with Cu K $\alpha$  radiation ( $\lambda=1.54$  Å). The images of transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were obtained on a FEI Tecnai G2 F20 at an accelerating voltage of 200 kV. electron spin resonance (ESR) spectra of the samples were investigated on a Bruker A300 spectrometer.

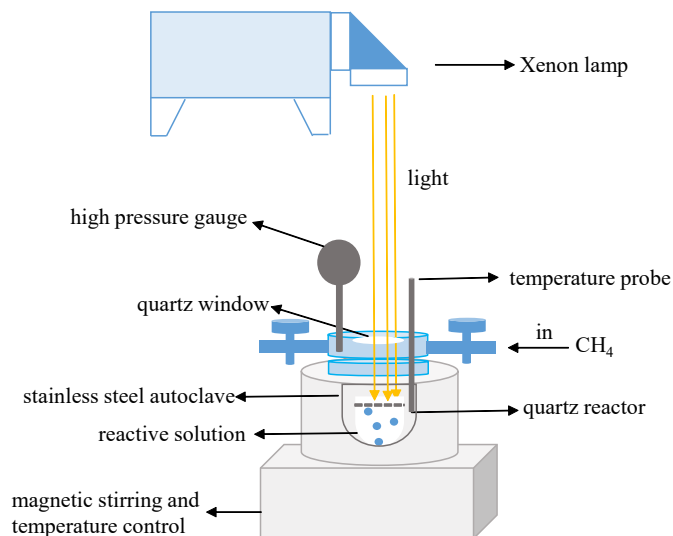
### **Photocatalytic coupling of methane**

The photocatalytic conversion of methane was performed in a stainless-steel batch reactor (~130 ml) with a quartz window on the top of the reactor and a Teflon vessel inside. The reactor could be put in a matched heating jacket which is used to keep temperature and to control magnetic stirring. The 300 W Xe lamp as light source was to simulate the solar light (100 mW/cm<sup>2</sup>). In a typical experiment, 20 mg catalyst (TiO<sub>2</sub>) and 20 ml DI water were added to a beaker, followed by addition of 0.1 ml HSO<sub>5</sub><sup>-</sup> aqueous solution (1 mol/L). Thereafter, the above suspension was placed into the visual autoclave reactor. Then, the reactor was purged with methane for several times to replace oxygen and air. The photocatalytic reaction was then carried out after injecting methane (2.0 MPa) under solar light irradiation at room temperature (around 25 °C). After photocatalytic reaction of methane for 1 h, the reactive system was cooled down

in ice-water bath for around 1 hour. The obtained products were analyzed by gas chromatography (GC, KECHUANG, GC2002) and high-performance liquid chromatography (HPLC, SHIMADZU, Essentia CTO-16). The GC was equipped with two flame ionization detectors (FID1 and FID2) and a thermal conductivity detector (TCD). We used GC to detect the gas-phase products, including alkane (such as CH<sub>4</sub>, CH<sub>3</sub>CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, etc.), over-oxidative products (CO, CO<sub>2</sub>), and by-products (H<sub>2</sub> and O<sub>2</sub>) by FID2 fixed a GDX-502 column (4m × 3mm), FID1 equipped with high temperature nickel converter for methanizer, and TCD connected to TDX-01 column (2m × 3mm), respectively. We used GC to detect the liquid products, including alcohol (such as CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, etc.) and aldehydes (such as CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>CHO, etc.), and ketones (such as CH<sub>3</sub>CH<sub>3</sub>CO) by FID2. The liquid organic hydrocarbon acids (e.g., CH<sub>3</sub>COOH, HCOOH, etc.) were analyzed on a HPLC. Notably, to quantify products accurately, their calibration curves were made in advance. Besides, acetylaceton color-developing method<sup>[1]</sup> was used to precisely detect HCHO produced after photocatalytic methane conversion. Actually, under acetic acid-ammonium acetate buffer solution (pH = 6), HCHO can react with acetylaceton and ammonia to form yellow-colored 3,5-diacetyl-1,4-dihydrolutidine, which demonstrates a characteristic UV-visible absorption at 413 nm. And the concentration of HCHO is proportional to the UV-visible absorption with peak intensity at 413 nm. Similarly, the comparative experiment with different oxidants including H<sub>2</sub>O<sub>2</sub> (10.2 μL), O<sub>2</sub> (0.5 MPa), CO<sub>2</sub> (0.5 MPa) were performed via the same photocatalytic procedure.

## Experimental Section

### *Experimental set-up for methane coupling*



### *ESR measurement*

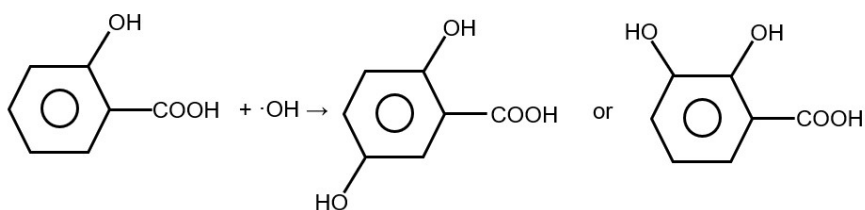
In the typical test, 20 mg Au<sub>1</sub>/WO<sub>3</sub> catalyst was dispersed in 20 ml deionized water, followed by stirring for 5 min. After that, 69  $\mu$ l peroxymonosulfate (HSO<sub>5</sub><sup>-</sup>, 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>) aqueous solution was added in the above suspension. Then, both 100  $\mu$ l 5-dimethyl-1-pyrroline N-oxide (DMPO) (100 mM) aqueous solution and above reactive suspension (100  $\mu$ l) were added into a capillary tube for •OH and SO<sub>4</sub><sup>-•</sup> measurement. For the measurement of •CH<sub>3</sub>, the reactive suspension (100  $\mu$ l) was obtained with the reaction with methane of 2 MPa for one hour in advance. After visible light irradiation for 5 min (a Xenon lamp fixed with UVCUT 420nm filter as light source), the typical •OH signal was collected. With the same procedure, 100  $\mu$ l DMPO (100 mM) methanol solution was used for •O<sub>2</sub><sup>-</sup> detection and 100  $\mu$ l 2,2,6,6-tetramethylpiperidine (TEMP) (100 mM) aqueous solution for <sup>1</sup>O<sub>2</sub> detection.

### *Trapping experiments*

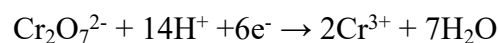
The trapping experiments of active species were implemented to study the mechanism process of photocatalytic conversion of methane. Here, 2 mmol of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, para-Quinone, salicylic acid, and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were adopted as the scavengers of e<sup>-</sup>, •O<sub>2</sub><sup>-</sup>, •OH, and h<sup>+</sup>, respectively.<sup>[2]</sup> Furfuryl alcohol (FFA) of 34.5 mmol was used as a scavenger

of  $^1\text{O}_2$ .<sup>[3]</sup> The below are the corresponding reactions between the scavengers and active species in details. We also cited the corresponding literature.

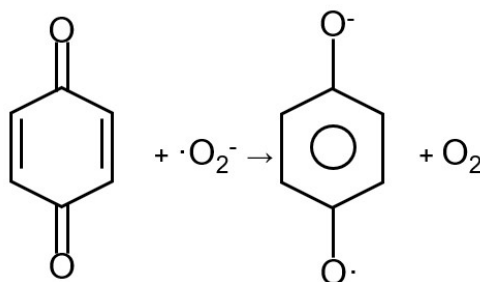
- 1) salicylic acid for  $\cdot\text{OH}$  trapping<sup>[4]</sup> :



- 2)  $\text{K}_2\text{Cr}_2\text{O}_7$  for electron ( $e^-$ ) trapping<sup>[5]</sup>:

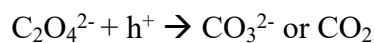


- 3) para-Quinone for superoxide radical ( $\cdot\text{O}_2^-$ ) trapping:<sup>[6]</sup>

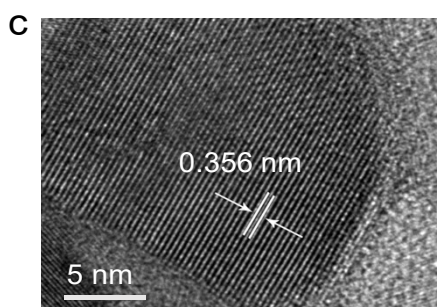
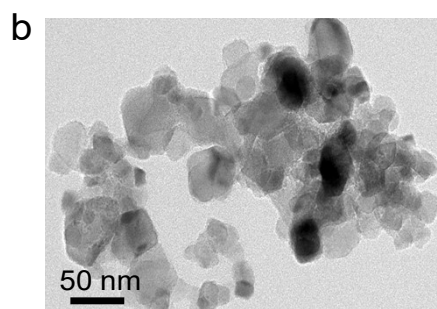
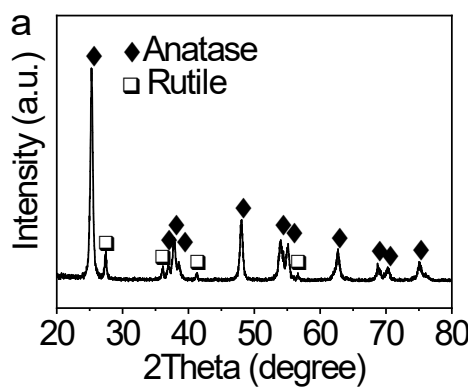
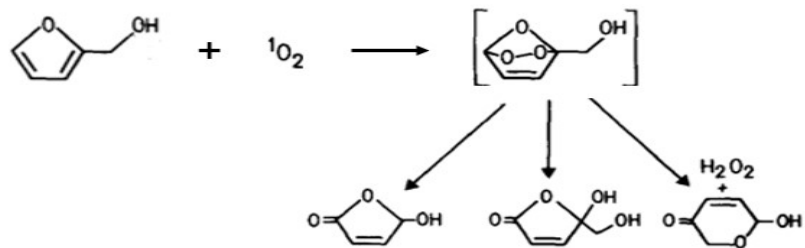


- 4)  $\text{Na}_2\text{C}_2\text{O}_4$  for holes ( $h^+$ ) trapping:<sup>[7]</sup>

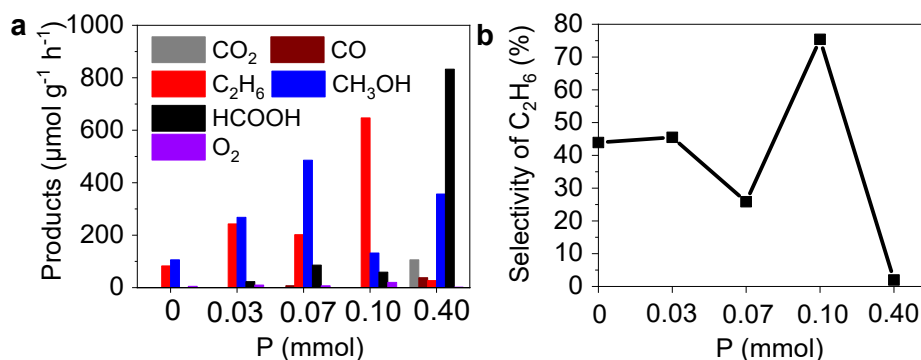
The  $\text{C}_2\text{O}_4^{2-}$  could be oxidized by photo-generated holes ( $h^+$ ) to  $\text{CO}_3^{2-}$  or  $\text{CO}_2$  based on literature as below reaction:



- 5) furfuryl alcohol for  $^1\text{O}_2$  trapping:<sup>[8]</sup>



**Figure S1.** Morphology and structure of  $TiO_2$  (Degussa P25) catalyst: (a) XRD patterns, (b) TEM, and (c) HR-TEM images



**Figure S2.** (a) Photocatalytic activity of methane oxidation and (b) corresponding selectivity of  $\text{CH}_3\text{CH}_3$  depending on different amounts of P.

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