

## Supporting Information

### **How Carbon Contamination on the Photocatalysts Interferes Performance**

#### **Analysis of CO<sub>2</sub> Reduction Reaction**

Jiakang You<sup>1</sup>, Mu Xiao<sup>1</sup>, Siqi Liu<sup>1</sup>, Haijiao Lu<sup>1</sup>, Peng Chen<sup>1</sup>, Zhi Jiang<sup>2</sup>, Wenfeng Shangguan<sup>2</sup>, Zhiliang Wang<sup>1\*</sup>, Lianzhou Wang<sup>1\*</sup>

Nanomaterials Centre, School of Chemical Engineering and Australian Institute for  
Bioengineering and Nanotechnology, The University of Queensland, St Lucia, Queensland,  
4072, Australia.

Email: [zhiliang.wang@uq.edu.au](mailto:zhiliang.wang@uq.edu.au); [l.wang@uq.edu.au](mailto:l.wang@uq.edu.au)

## **Materials**

TiO<sub>2</sub> (Sigma-Aldrich, P25 21 nm primary particle size (TEM),  $\geq 99.5\%$  trace metals basis), and HAuCl<sub>4</sub> · 3H<sub>2</sub>O (Sigma-Aldrich, ACS reagent,  $\geq 49.0\%$  Au basis), NaBH<sub>4</sub> (Sigma-Aldrich, caplets, 98%), CuSO<sub>4</sub> (Sigma-Aldrich,  $\geq 99\%$ ), Melamine (Sigma-Aldrich,  $\geq 99\%$ ), NaOH (Sigma-Aldrich,  $\geq 98\%$ ), Bi<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich,  $\geq 99.9\%$ ), V<sub>2</sub>O<sub>5</sub> (Thermo Fisher Scientific,  $\geq 99.6\%$ ), SnO<sub>2</sub> (Sigma-Aldrich,  $\geq 99.9\%$ ), nitric acid (Thermo Fisher Scientific, 70%), ethanol (Merk EMSURE<sup>®</sup> absolute for analysis), and ethyl acetate (Sigma-Aldrich, anhydrous, 99.8%) were used without further purification. Deionised (DI) water was used throughout the experiment.

## **Synthesis of CuO photocatalyst**

CuO was prepared using a modified method previously reported.<sup>1</sup> In this process, CuSO<sub>4</sub> (0.81 g) was dissolved in DI water (50 mL) under vigorous stirring at 60 °C for 5 mins to form solution A. NaOH (1.2 g) was dissolved in DI water (5 mL) to form solution B. Solution B was then added dropwise to solution A. Next, the dark precipitate was stirred for another 10 mins, and then cooling to room temperature naturally. Afterwards, the supernatant was removed. The precipitates with CuO particles were centrifuged three times in DI water and dried in an oven at 70 °C overnight.

## **Synthesis of BiVO<sub>4</sub> photocatalyst**

BiVO<sub>4</sub> was prepared using a method previously reported.<sup>2</sup> Bi<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> were mixed in 0.5 M nitric acid solution at a molar ratio of 1:1. The mixture was then stirred at ambient condition for 96 hours. Afterwards, the BiVO<sub>4</sub> particles were centrifuged and washed three times in DI water and dried in an oven at 70 °C overnight.

### **Synthesis of g-C<sub>3</sub>N<sub>4</sub> photocatalyst**

In a typical synthesis procedure, 20 g of melamine was put into an alumina crucible with a lid and calcined to 550 °C in air for 2 hours. After calcination, g-C<sub>3</sub>N<sub>4</sub> was obtained.

### **All inorganic deposition of gold nanoparticles on photocatalysts (TiO<sub>2</sub>, CuO, BiVO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>, and SnO<sub>2</sub>)**

Gold was deposited using a modified all-inorganic method previously reported.<sup>3</sup> First, 1.0 g photocatalyst (TiO<sub>2</sub>, CuO, and BiVO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>, SnO<sub>2</sub>) was dispersed in 100 mL DI water. After 30-min ultrasonic treatment, 5 mL HAuCl<sub>4</sub> solution (2 mgAu/mL) was added into the dispersion. Then, 2.539 mL of the 0.1 M freshly prepared solution of NaBH<sub>4</sub> was added into the dispersion under vigorous stirring. After 10-min stirring, the solution was centrifuged and washed thoroughly with DI water for three times. The final product was obtained after drying in the oven at 70 °C overnight. Afterwards, all the as-synthesised materials (except g-C<sub>3</sub>N<sub>4</sub>, as it is carbon containing material) decorated with gold nanoparticles were heated at 450 °C under air for 2 hours.

### **Characterisation**

X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) with an Al K $\alpha$  X-ray radiation source was used to characterise the chemical composition of the material. The UV-vis absorption spectra were obtained using a JASCO V-650 spectrophotometer. The crystalline phase of the samples was characterised by X-ray powder diffraction (Rigaku, Miniflex, benchtop powder XRD instrument) with Cu K $\alpha$  ( $\lambda=0.15406$  nm) radiation. A transmission electron microscope (Hitachi HT 7700 120kV TEM) is used to observe the gold nanoparticle distribution on the P25.

### **Analysis method for UPS**

The UPS data was analysed according to the literature.<sup>4</sup> The work functions (WF) of the samples were obtained by subtracting the cutoff binding energy ( $E_{cutoff}$ ) with the radiative photon energy (He I  $\alpha$  at 21.22 eV). The distance between WF and valence band (VB) edge was defined as  $E_{VBM}$ . The VB edges of different photocatalysts (TiO<sub>2</sub>, CuO and BiVO<sub>4</sub>) can be acquired by using the following equations S1 and S2:

$$WF = E_{cutoff} - 21.22 \text{ eV} \quad (1)$$

$$VB = WF - E_{VBM} = E_{cutoff} - 21.22 \text{ eV} - E_{VBM} \quad (2)$$

Combining the bandgap value ( $E_g$ ) acquired from the UV-vis absorption spectra, the conduction band (CB) edges of photocatalysts can be obtained by using the following equation S3:

$$CB = E_g + VB = E_g + E_{cutoff} - 21.22 - E_{VBM} \quad (3)$$

### **Photocatalytic performance test**

Firstly, 12.5 mg Au/P25 was spread on the home-made glass holder. The glass holder with Au/P25 was baked at 100 °C for 30 mins prior to the photocatalytic performance test. Then, the glass holder was put in a metal reactor (purchased from Perfectlight Technology Co., Ltd, Beijing). 1 mL DI water was added into the reactor as the reductant. The reactor was then sealed and purged with argon gas for 30 mins. After that, high-purity CO<sub>2</sub> was purged for 30 mins. Before illumination, 1 mL of the gas from the reactor was injected into the gas chromatography (GC-2014, Shimadzu) to record the background information. The reactor was illuminated by a 300 W Xe lamp (lamp current:19 A, full spectrum, Perfectlight Technology Co., Ltd). The impact of organic solvent vapour (i.e.,) was investigated by adding 1  $\mu$ L of ethanol the reactor.

### **Oxygen Plasma Treatment**

The plasma cleaning provides nanoscale surface cleaning of materials for various applications. In this work, O<sub>2</sub> plasma treatment is used to remove contaminants (especially carbon-based species) from the surface of photocatalysts. In detail, the photocatalyst loaded on a glass support is put into the chamber of the Harrick Plasma expanded plasma cleaner (PDC-001 and PDC-002) with a power of 30 W for 30 minutes.

### Supporting Figures

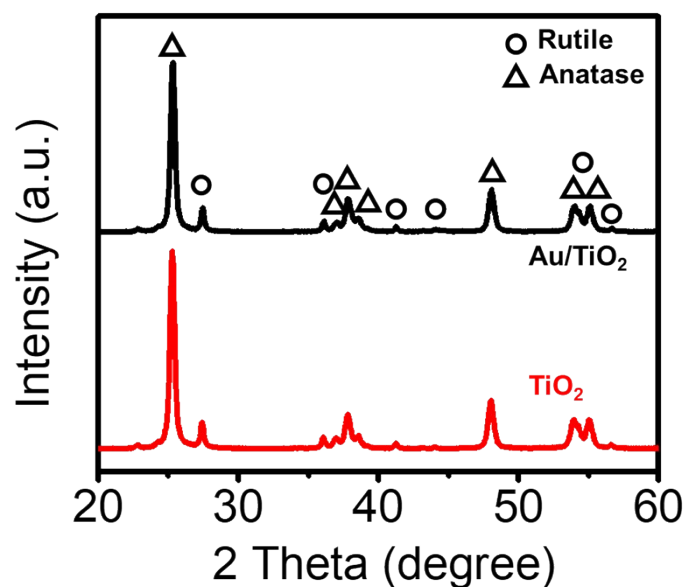


Figure S1. XRD pattern of Au/TiO<sub>2</sub> (P25) and TiO<sub>2</sub> (P25).

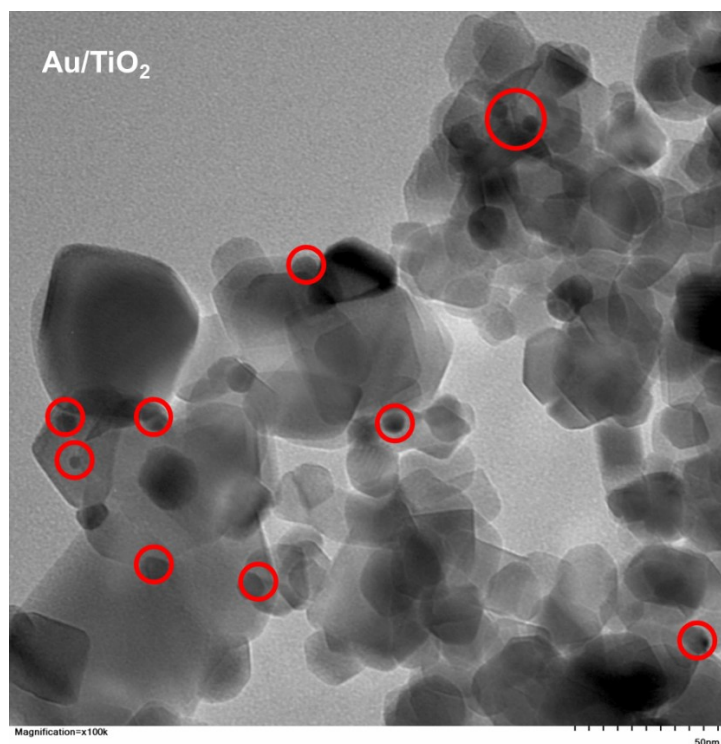


Figure S2. TEM image of Au/TiO<sub>2</sub>. Gold nanoparticles were indicated by red circles.

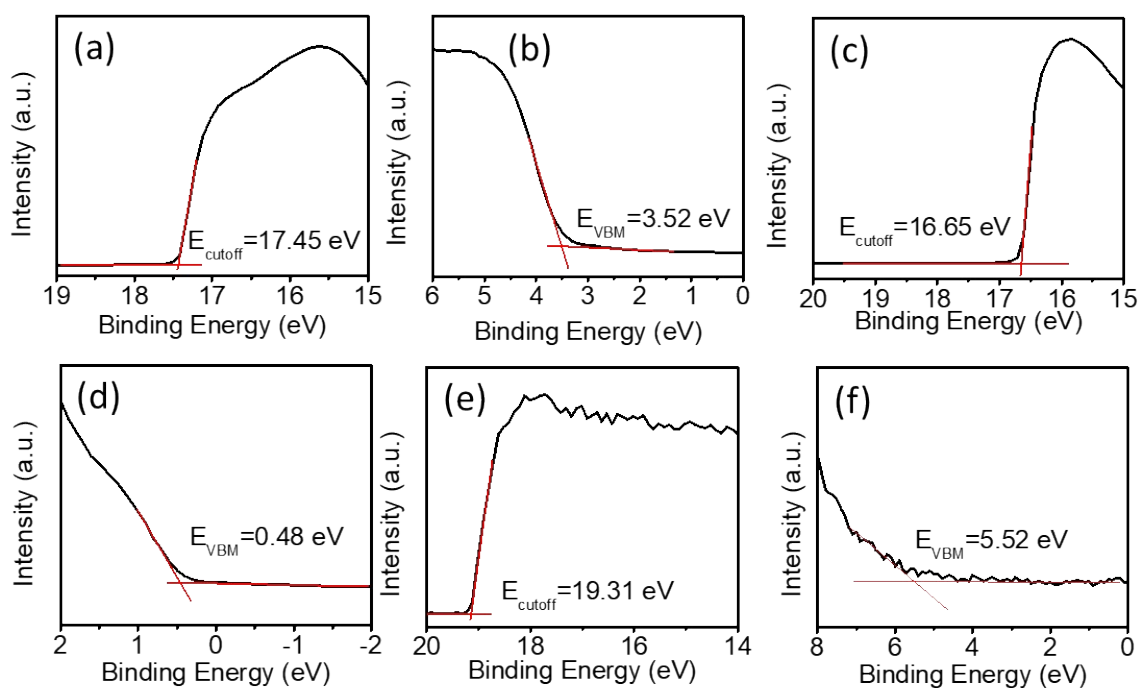


Figure S3. UPS spectra of (a)-(b) TiO<sub>2</sub> (P25), (c)-(d) CuO, (e)-(f) BiVO<sub>4</sub>.

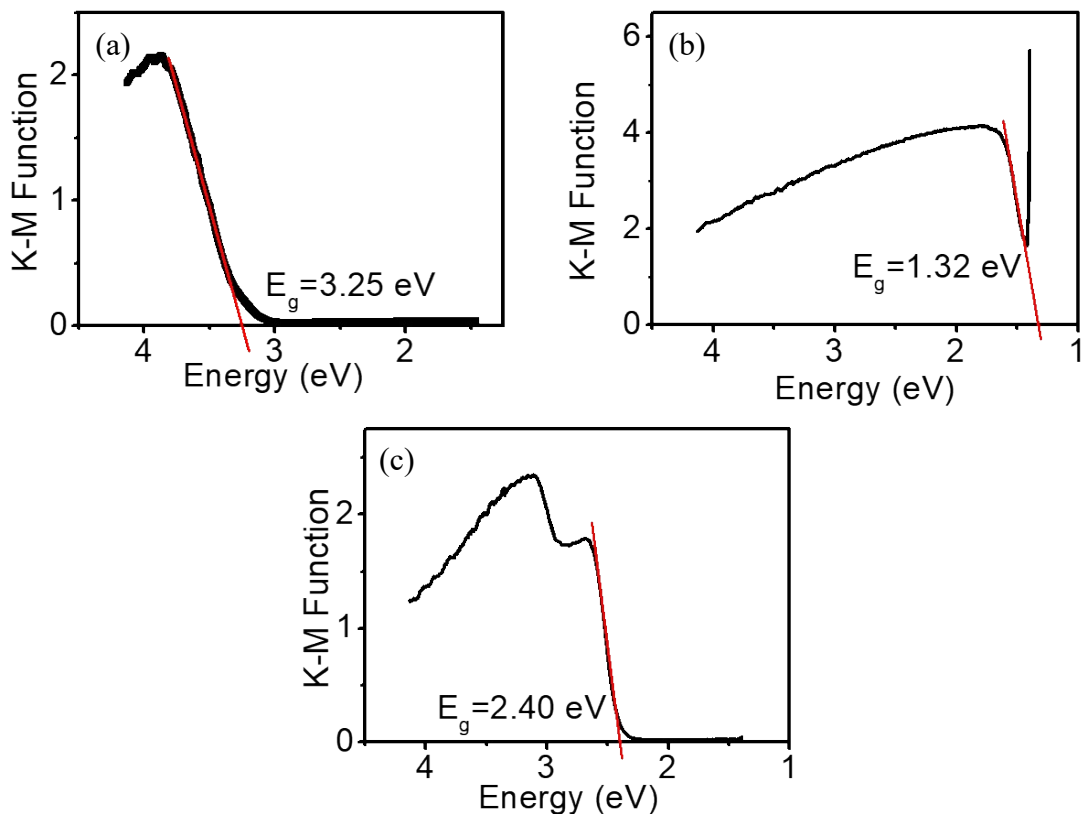


Figure S4. Determining the band gap of (a)  $\text{TiO}_2$  (P25), (b)  $\text{CuO}$ , and (c)  $\text{BiVO}_4$  by K-M function.

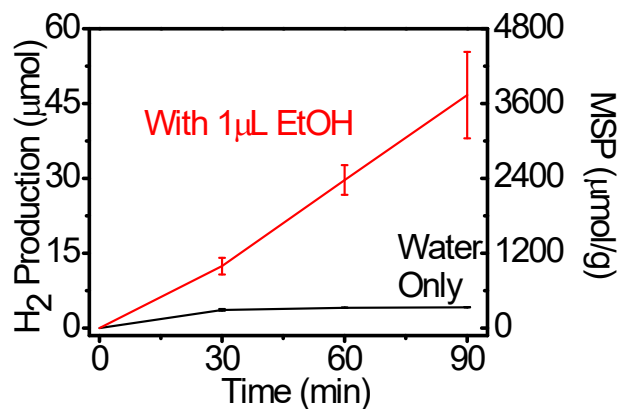


Figure S5. Photocatalytic performance of  $\text{Au/TiO}_2$  with different solvents: Hydrogen production. MSP: Mass Specific Production Rate.

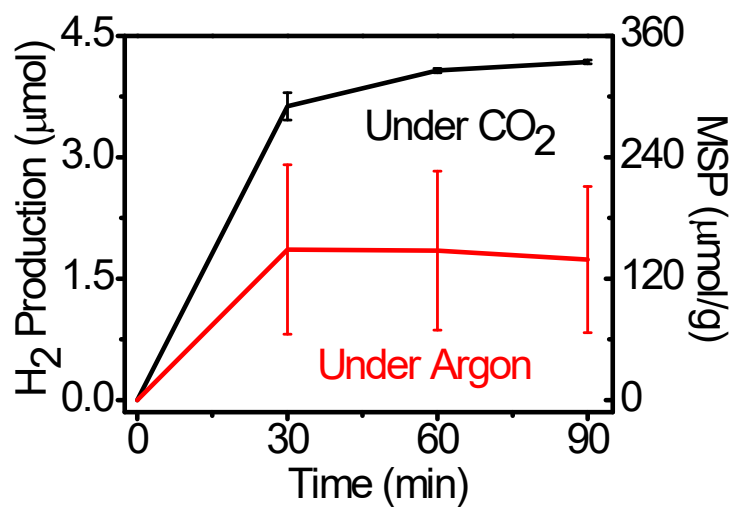


Figure S6. Controlled experiments under argon and CO<sub>2</sub> atmospheres: Hydrogen production. MSP: Mass Specific Production Rate.

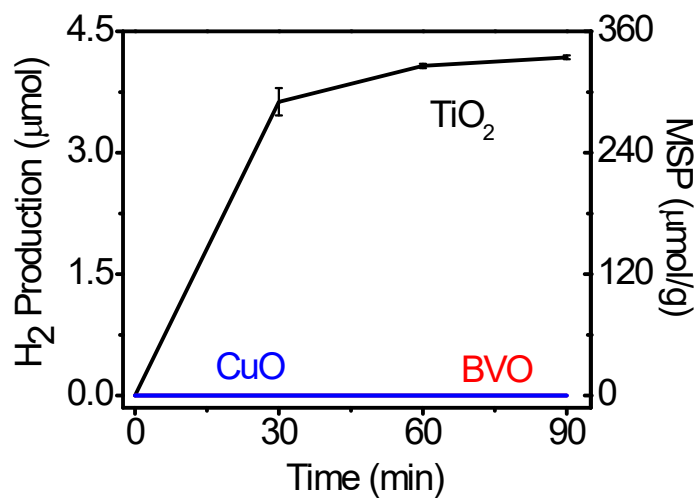


Figure S7. Photocatalytic CO<sub>2</sub>RR performance over TiO<sub>2</sub>, CuO and BVO: Hydrogen production. MSP: Mass Specific Production Rate.



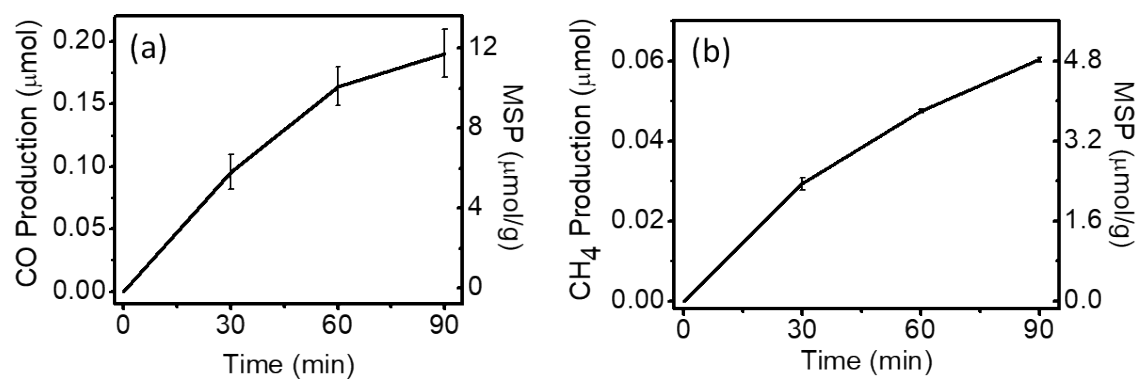


Figure S8. Photocatalytic CO<sub>2</sub>RR performance of SnO<sub>2</sub> (a) CO production; (b) CH<sub>4</sub> production. (No hydrogen production was detected.) MSP: Mass Specific Production Rate.

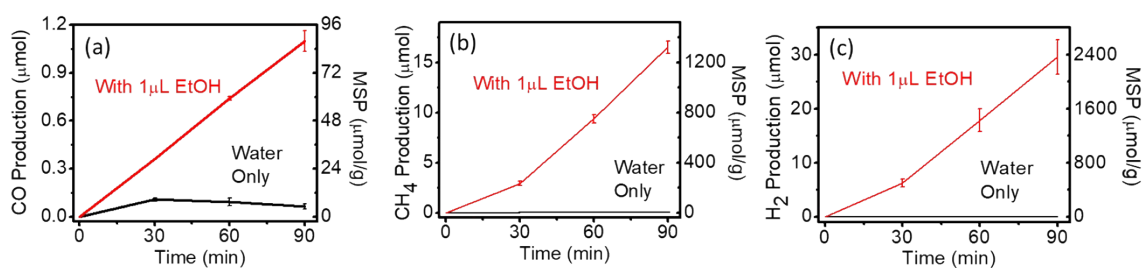


Figure S9. Photocatalytic performance of pure TiO<sub>2</sub> with different solvents (a) CO production; (b) CH<sub>4</sub> production; and (c) H<sub>2</sub> production. MSP: Mass Specific Production Rate.

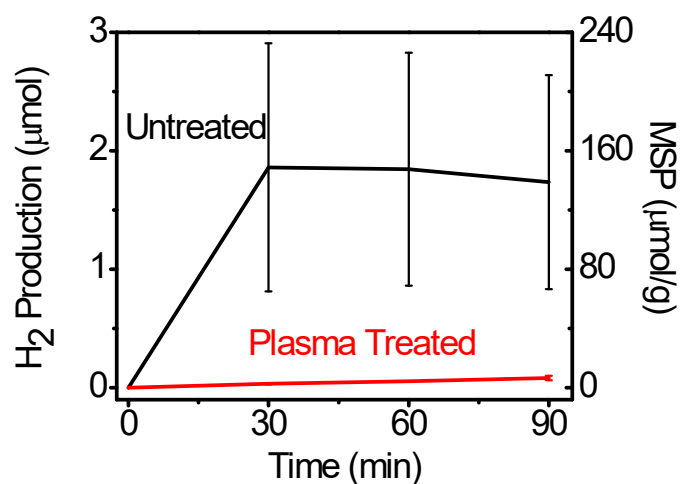


Figure S10. Controlled experiments before and after plasma treatment under argon and CO<sub>2</sub> atmospheres: Hydrogen production. MSP: Mass Specific Production Rate.

Table S1. Surface carbon content of TiO<sub>2</sub>, CuO, and BiVO<sub>4</sub> based on XPS survey scan.

| Material               | Surface carbon content At% | Surface carbon content wt% |
|------------------------|----------------------------|----------------------------|
| TiO <sub>2</sub> (P25) | 27.21                      | 14.96                      |
| CuO                    | 38.74                      | 26.02                      |
| BiVO <sub>4</sub>      | 34.88                      | 8.44                       |

Table S2. Selectivity analysis of CO, CH<sub>4</sub>, and H<sub>2</sub> with different solvents for Au/TiO<sub>2</sub>.

| Selectivity     | Water only     | With 1 μL EtOH |
|-----------------|----------------|----------------|
| CO              | 4.54% ± 0.58%  | 0.2% ± 0.02%   |
| CH <sub>4</sub> | 42.17% ± 5.35% | 57.03% ± 0.12% |
| H <sub>2</sub>  | 53.29% ± 5.93% | 42.76% ± 0.10% |

## References

1. R. Li, X. Tao, R. Chen, F. Fan and C. Li, *Chem. Eur. J.*, 2015, **21**, 14337-14341.
2. H. Wu, R. Irani, K. Zhang, L. Jing, H. Dai, H. Y. Chung, F. F. Abdi and Y. H. Ng, *ACS Energy Lett.*, 2021, **6**, 3400-3407.
3. M. V. Dozzi, L. Prati, P. Canton and E. Selli, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7171-7180.
4. P. Chen, Z. Wang, S. Wang, M. Lyu, M. Hao, M. Ghasemi, M. Xiao, J.-H. Yun, Y. Bai and L. Wang, *Nano Energy*, 2020, **69**, 104392.