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How carbon contamination on the photocatalysts interferes with the performance analysis of CO₂ reduction†

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Photocatalytic carbon dioxide (CO₂) reduction reaction (CO₂RR) for the production of valuable chemicals is a promising solar-driven strategy to mitigate CO₂ emissions. However, carbon contamination on the photocatalysts interferes with the investigation of CO₂RR performance. This work quantitatively investigates the significant impact of carbon contamination on performance analysis of photocatalytic CO₂RR, which can lead to false-positive results of photocatalysts with different types of band structure (*i.e.*, TiO₂, CuO, and BiVO₄) due to photoinduced oxidation process. Moreover, the commonly used organic solvent in a laboratory environment (*e.g.*, ethanol) was proved to have a profound impact on photocatalytic CO₂RR behaviour wherein 1 microliter of ethanol could boost the apparent methane generation by 17 times. To solve this issue, oxygen plasma treatment is demonstrated to be effective in removing surface carbon contamination. To minimise the impact of surface carbon contamination and eliminate false-positive results, it is expected to further enhance the photocatalytic performance and store catalysts in a carbon-free atmosphere.

The rapid consumption of fossil fuels in human activities, such as transport, industry, and household sectors, causes a striking increase in CO₂ concentration in the atmosphere, leading to serious environmental issues, such as global warming and ocean acidification.^{1,2} Thus, these problems must urgently be addressed by reducing CO₂ emissions and making full utilisation of the existing CO₂. Photocatalytic CO₂ reduction reaction (CO₂RR) has attracted global research interest over the past decades.³ In an ideal process, it is expected that the photo-generated electrons in the photocatalysts are applied to reduce

CO₂, meanwhile, photogenerated holes are consumed for water oxidation. Considering the stable structure of CO₂ with a high bond energy of 750 kJ mol⁻¹,⁴ there is a high energy barrier for the activation of CO₂, which requires sophisticated photocatalyst designs.

Despite tremendous research efforts, the production rates of carbon monoxide (CO) and methane (CH₄), which are the most common products, stay at low levels (*e.g.*, <17.33 μmol g⁻¹ h⁻¹ for CO and <2000 μmol g⁻¹ h⁻¹ for CH₄).⁵⁻¹² However, external factors, such as organic vapours in a lab, surface carbon contamination, *etc.*, are more likely to produce these carbon products *via* oxidation reaction, other than CO₂ reduction, and therefore they might result in false-positive signals. For example, methanol (CH₃OH), a common hole scavenger in photocatalytic reactions, can produce significant amounts of CO through a photocatalytic oxidation process.¹³⁻¹⁶ Although isotope analysis is regarded as an effective approach to verify the carbon source by tracing the ¹³C transfer from CO₂ molecules to the products, the possible isotopic substitution makes this method less reliable.¹⁷⁻²⁰ To provide reproducible and convincing data for CO₂RR analysis, some recent perspectives invoked the elimination of contamination sources as completely as possible.^{21,22} Yet, there is still no quantitative investigation on how carbon contamination interferes with the performance analysis of photocatalytic CO₂RR.

In this work, we have provided a quantitative analysis of the apparently over-estimated product amount due to hole-induced contamination oxidation, other than the CO₂RR process. Photocatalysts with different valence band (VB) positions have been applied to verify that the contamination oxidation reaction exaggerates the apparent CO₂RR activity. Using a prototypical Au/TiO₂ photocatalyst for CO₂RR, introducing a trace amount (*i.e.*, 1 μL) of ethanol (EtOH) caused over 17 times higher CH₄ production rate and higher stability for CO production. Moreover, facile oxygen plasma pre-treatment was confirmed to be an effective protocol to minimise the influence of carbon contamination during gas-phase photocatalytic CO₂ conversion. These findings provide new insights into CO₂RR research

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and will enable the acquisition of more consistent and reliable quantitative results across the research community.

The Au/TiO₂ has been intensively investigated to be an effective photocatalyst for CO₂RR, which makes it a good benchmark for investigating the carbon contamination issue. The prototypical Au/TiO₂ photocatalysts have been widely reported to be active towards gas-phase CO₂ conversion to CO and CH₄, with a production rate ranging from 3 to 210 μmol g⁻¹ h⁻¹ depending on reaction conditions.^{5,23} Considering the ultralow dosage of photocatalyst (*c.a.* 10 mg) in the reported research, the absolute yields of CO₂RR products are negligible. In our research, we adopted a similar procedure to coat the as-prepared Au/TiO₂ photocatalyst (ESI†) on a glass substrate with a rough surface. Herein, Au was deposited *via* chemical reduction by sodium borohydride to avoid introducing organic sources on the TiO₂ surface.^{24–26} The X-ray diffraction (XRD) (Fig. S1†) and transmission electronic microscopy (TEM) (Fig. S2†) of the as-produced Au/TiO₂ indicate that the Au nanoparticles were deposited on the TiO₂ surface.

Photocatalytic CO₂ conversion was carried out in a batch reactor, wherein the system was filled with pure CO₂ (>99.9%) before turning on the lighting (ESI†). Fig. 1a and b show the CO and CH₄ with a mass-specific production (MSP) of 30 μmol g⁻¹ and 67.5 μmol g⁻¹, respectively, in 90 minutes. This photocatalytic activity is comparable to literature results based on similar Au/TiO₂ systems.^{27–31} Unexpectedly, in the controlled experiment, where the photocatalytic system was filled with argon gas (Ar), obvious CH₄ and CO production was also detected. Especially, the absolute yields of CH₄ were very close to the case in the presence of CO₂, indicating that the apparent CO₂RR activity has been overestimated as shown in Fig. 1b. In addition, profound H₂ production (Fig. S3†) was observed in both cases (while no oxygen was detected), which may lead to a noticeable CO decrease as shown in Fig. 1a *via* hydrogenation. With the above results, there is a question on the origin of CO and CH₄ under an Ar atmosphere.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface chemical environment of TiO₂ (Fig. 1c). Although we avoided the organic sources during photocatalyst preparation, the carbon peak could always be observed even on the pure inorganic metallic samples, which is indexed to ubiquitous carbon contamination from air exposure.³² This peak is commonly used as a reference value to calibrate XPS

data, representing C–C or C–H bond.^{32–34} These carbon species can produce extra CO or CH₄ with the interaction with the photogenerated charges.

The applied TiO₂ holds a large bandgap, where it is capable of producing CO and CH₄ either by CO₂ reduction reaction or *via* carbon contamination oxidation. To get more insight into whether photogenerated electrons or holes contribute more to the CO and CH₄ generation, the other two semiconductors, BiVO₄ and CuO, were selected due to their band structure features (Fig. 2a, see ESI† for details on preparation). Ultraviolet photoelectron spectroscopy (UPS) and ultraviolet-visible (UV-vis) spectroscopy were used to further determine the band positions as shown in Fig. S4 and S5.† The properties of the valence band (VB) and conduction band (CB) of BiVO₄, CuO, and TiO₂ are summarised in Fig. 2a, which shows the CB of CuO and VB of BiVO₄ to be close to the CB and VB of TiO₂, respectively, in accordance with the literature.^{35–37} From the relative position of CB (–3.73 eV) to the redox potential of CO₂/CO (–4.38 eV) and CO₂/CH₄ (–4.67 eV), it can be concluded that only CuO can facilitate the CO₂RR. While the relatively shallow VB (–5.05 eV) of CuO makes it unlikely to process contamination oxidation. The BiVO₄ has the opposite situation in that CO₂RR is unlikely to happen due to the thermodynamic limit of CB (–5.03 eV), but the contamination oxidation process is relatively easy due to the deep VB (–7.43 eV). Therefore, the photocatalytic performance of CuO and BiVO₄ can help distinguish whether the CO₂RR or oxidation of carbon contaminations contributes to the apparent CO and CH₄ generation. Surface carbon content on the TiO₂, CuO, and BiVO₄ was determined to be 14.96, 26.02, and 8.44 wt%, respectively, as analysed by XPS (Table S1†).

Their photocatalytic performance is shown in Fig. 2b and c and S7.† Interestingly, BiVO₄ produced significant amounts of CH₄ (5.4 μmol g⁻¹) and CO (13.5 μmol g⁻¹), while CuO produced nearly null. As mentioned above, products from BiVO₄ indicate that carbon contamination oxidation occurs, which can lead to false-positive CO₂RR results, despite the consensus that BiVO₄ is not capable of this process. Another photocatalyst, SnO₂, also possesses a low CB which is challenged for CO₂RR.³⁸ However, a considerable amount of CH₄ (3.8 μmol g⁻¹) and CO (13.1 μmol g⁻¹) is observed upon light irradiation (Fig. S8†). We suppose this is also a false-positive result for CO₂RR caused by carbon contamination oxidation. The absence of a product from CuO

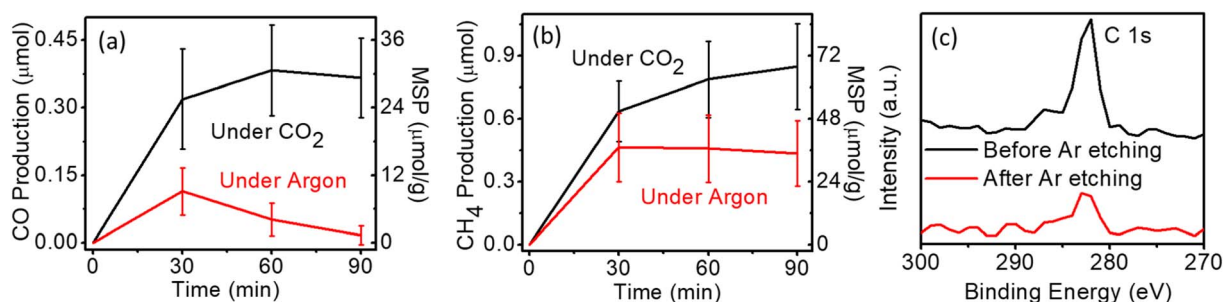


Fig. 1 (a) CO production and (b) CH₄ production from photocatalytic reactions on Au/TiO₂ in CO₂ (black line) or Ar (red line). (c) Comparison of C 1s XPS spectrum of the same TiO₂ sample before and after Ar etching. MSP: mass-specific production.



Fig. 2 (a) Band position of TiO₂, CuO, and BiVO₄ in line with CO₂RR, redox potentials of hydrogen and oxygen evolution reactions. Photocatalytic CO₂RR performance over TiO₂, CuO, and BiVO₄ (b) CO production; (c) CH₄ production. MSP: mass-specific production.

further indicates the significance of the oxidation process for the apparent CO and CH₄ generation.

Carbon-containing photocatalysts have been extensively researched for CO₂RR because of their attractive physico-chemical properties. Graphitic carbon nitride (g-C₃N₄) is one of the most investigated metal-free organic photocatalysts due to its low cost, visible light harvesting, and suitable band position

for CO₂RR.³⁹ However, the carbon in g-C₃N₄ will interfere with the CO₂RR performance analysis. Fig. 3 shows the photocatalytic performance on g-C₃N₄ under Ar and CO₂ atmospheres. The production rates of CO (47.1 μmol g⁻¹) and CH₄ (3.5 μmol g⁻¹) under the Ar atmosphere have very small and even negligible difference, as compared to the rates under the CO₂ atmosphere. These results are consistent with the report of

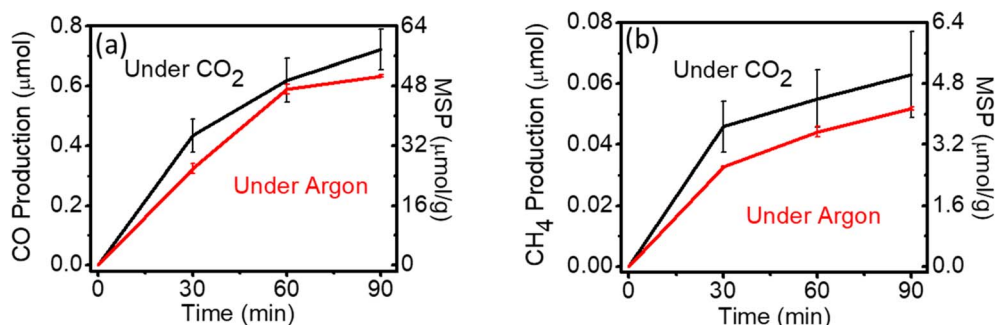


Fig. 3 (a) CO production and (b) CH₄ production from photocatalytic reactions on g-C₃N₄ in CO₂ (black line) or Ar (red line). MSP: mass-specific production.

light-induced self-decomposition of $g\text{-C}_3\text{N}_4$, rather than CO_2RR .⁴⁰ Theoretical calculations have indicated that self-decomposition reaction is thermodynamically more favourable than CO_2RR .⁴⁰

The impact of organic pollution on photocatalytic CO_2RR is even more pronounced in the presence of ethanol (EtOH), which is a widely used organic solvent for synthesis and a sacrificial agent for photocatalysis. Take the Au/ TiO_2 system as an example, when 1 μL of EtOH is deliberately added to the reaction system, the CH_4 production rate was boosted by 17 times from 68 $\mu\text{mol g}^{-1}$ to 1244.8 $\mu\text{mol g}^{-1}$ as shown in Fig. 4a because of the alcohol and carboxyl acid decomposition under the light.^{41–45} Meanwhile, a large amount of hydrogen was produced (Fig. S7[†]), which could inhibit the generation of CO as shown in Fig. 4b. The photocatalytic performance of pure TiO_2 was also evaluated as a reference (Fig. S9[†]), which showed overall lower activity in the absence of Au cocatalyst. A plausible pathway for EtOH oxidation under light is shown in Fig. 4c. Upon light irradiation, ethanol was oxidised to ethanal with hydrogen generation. Ethanal can be decomposed *via* three different routes to mislead the photocatalytic CO_2RR test. Ethanal can be directly converted to CO_2 and hydrogen *via* the photocatalytic process. Under ambient conditions, some of the ethanal decomposes to produce CH_4 and CO spontaneously.

While, in some cases, the above products would be further oxidised to acetic acid and H_2 with acetic acid being further decomposed to CH_4 and CO_2 upon light illumination. Thus, the introduction of EtOH into the reaction system not only affects the activity analysis, but also influences the selectivity analysis (Table S2[†]) with considerable hydrogen production (Fig. S7[†]). Therefore, possible false-positive results can be obtained due to the organic residuals in the system, which must be eliminated when conducting photocatalytic CO_2RR experiments. Due to the dramatic performance boost by the trace amount of EtOH, researchers in this field should be extremely careful about organic solvent vapours generated in the laboratory environment.

Oxygen plasma treatment is commonly used to eliminate residual organic ligands from the material surface. To avoid the interference of surface contamination, oxygen plasma cleaning was performed to etch the surface of the photocatalyst (*i.e.*, Au/ TiO_2). Fig. 5 and S10[†] show the photocatalytic performance of treated Au/ TiO_2 photocatalysts. In the Ar environment, the CO and CH_4 production rates decreased dramatically to a negligible level, especially for CH_4 ; the production rate for CH_4 dropped from 34 to 4.69 $\mu\text{mol g}^{-1}$, indicating the effectiveness of the oxygen plasma treatment. Therefore, oxygen plasma treatment can be used to effectively clean the surface of the materials

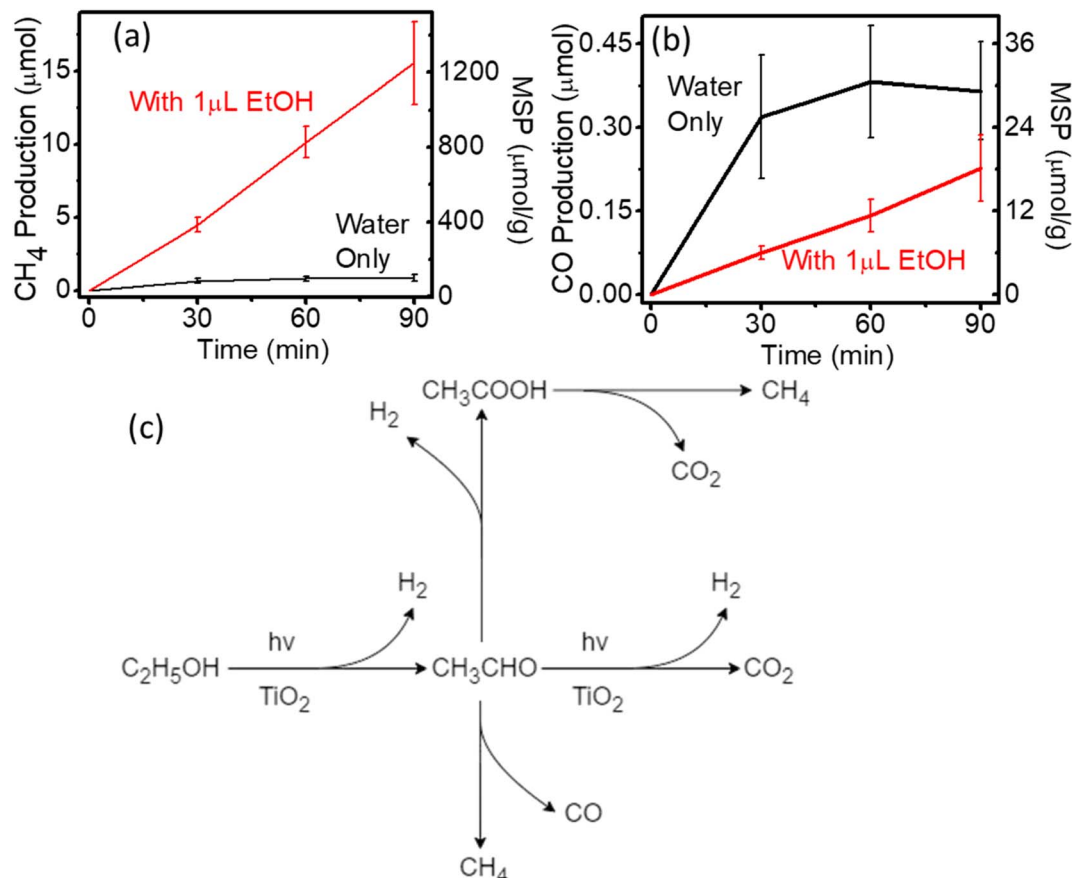


Fig. 4 Photocatalytic performance of Au/ TiO_2 with different solvents (a) CO production; (b) CH_4 production. (c) Schematic illustration of photocatalytic ethanol oxidation. MSP: mass-specific production.

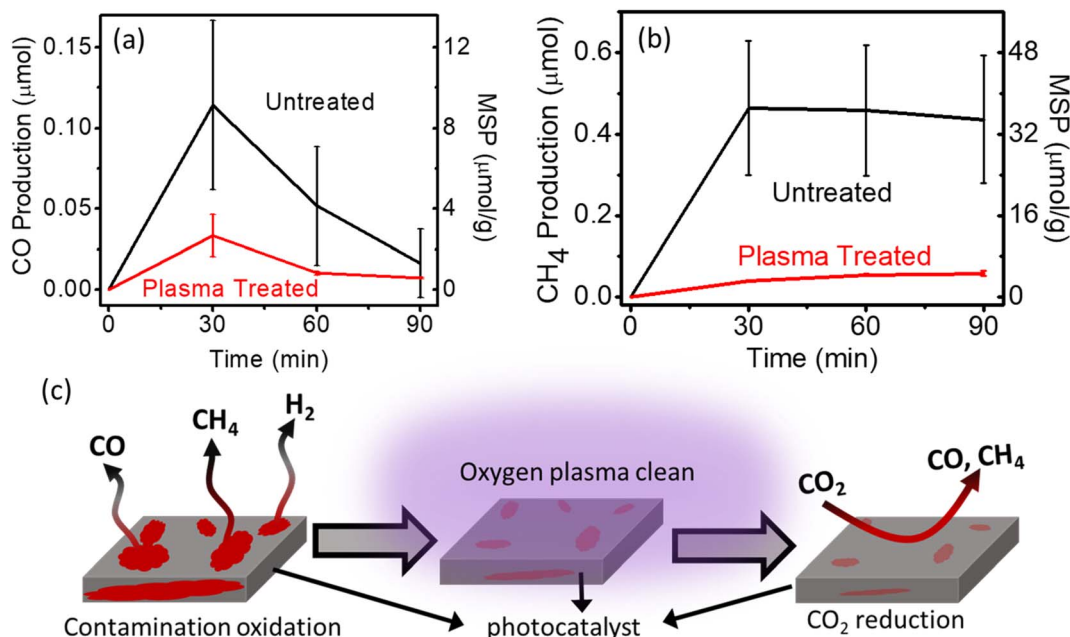


Fig. 5 Controlled experiments before and after plasma treatment under the Ar atmosphere (a) CO production; (b) CH₄ production. MSP: mass-specific production rate. (c) schematic representation of oxygen plasma cleaning.

before conducting photocatalytic experiments as shown in Fig. 5c.

In summary, we have quantitatively shown the influence of carbon contamination on photocatalysts during photocatalytic CO₂RR activities. When the photocatalytic CO₂RR activity is low, the impact of the carbon contamination oxidation is therefore significant. The commonly used organic solvent in laboratories (e.g., ethanol) was demonstrated to have a serious impact on photocatalytic CO₂RR behaviour, leading to false-positive results. To address this issue, oxygen plasma treatment is effective in removing carbon contamination by cleaning the surface of the materials before conducting photocatalytic experiments. The reason for such a significant impact of carbon contamination is the extremely low production rate and carbon conversion rates of photocatalytic CO₂RR.^{46–49} If the production and carbon conversion rates are high enough (e.g., >10 mmol g⁻¹ h⁻¹), the carbon contamination issue would be negligible. Some strategies can be utilised for higher CO₂RR performance, such as defect engineering, nanostructure design, cocatalysts design, heterostructure design, and Z-scheme construction. Furthermore, photocatalysts should be stored in a carbon-free environment (e.g., an N₂/Ar-filled glove box), if possible, to minimise carbon contamination. Long-term stability tests could decrease the effect of carbon contaminations. Future research should focus on improving the production rate and selectivity and developing highly efficient photocatalysts for CO₂RR.

Conflicts of interest

There are no conflicts to declare.

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