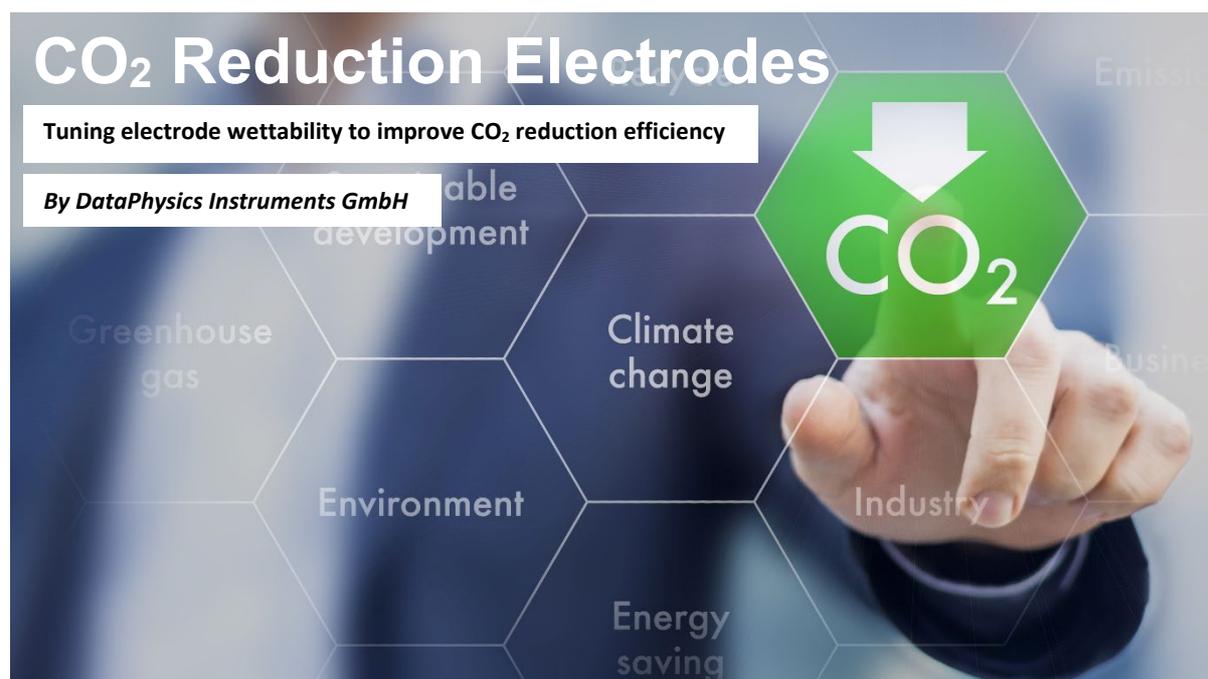


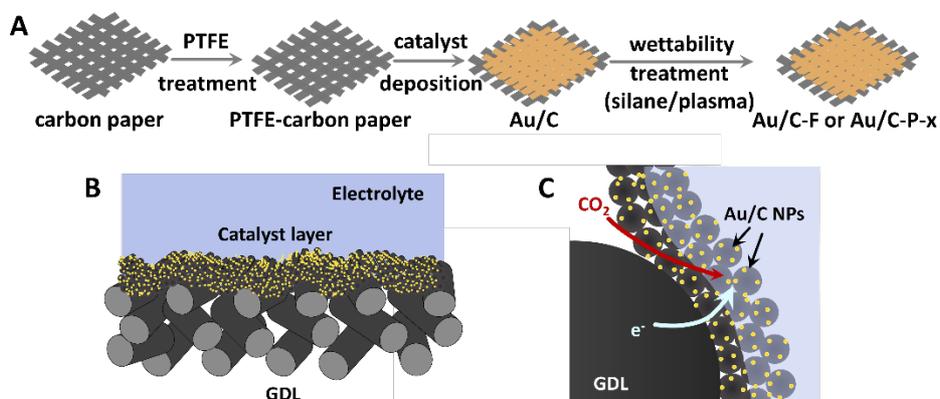
How contact angle measurements help to achieve efficient electrochemical CO<sub>2</sub> reduction.



CO<sub>2</sub> emissions are the crucial driver of global climate change. To reduce CO<sub>2</sub> emissions, various approaches have been developed to capture CO<sub>2</sub> and transform it into commodity chemicals (e.g. CO) or hydrocarbon fuels, including the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). To increase the CO<sub>2</sub>RR efficiency, scientists are now focusing on three-phase contact (TPC) systems instead of liquid–solid double phase contact (DPC) system due to advantages of TPC systems for electrochemical CO<sub>2</sub> reduction. One of the most significant advantages is the higher diffusion coefficient of CO<sub>2</sub> in the gas phase, allowing the use of high pH electrolytes. In spite of great progress in electrochemical catalyst design, studying gas–liquid–solid three-phase interfaces is still quite challenging due to the limited knowledge about interfacial structures and CO<sub>2</sub> transportation under non-equilibrium conditions. In addition, it is well-known that the wettability of gas–liquid–solid interfaces has huge impact on electrochemical reactions on the electrodes by affecting the gas diffusion and electron transfer processes. However, the critical influence of interfacial wettability on the CO<sub>2</sub>RR remains largely unexplored. Therefore, more and more researchers are interested in the studies of interfacial wettability of TPC systems. Besides, gold-based nanostructures are getting an increased attention due to their advantages in providing an efficient CO<sub>2</sub>RR and a highly selective CO production. Recently Shi et al. have revealed the crucial role of wettability-controlled interfacial structures in promoting the interfacial CO<sub>2</sub> transportation and CO<sub>2</sub>RR efficiency. They illustrated that a Cassie-Wenzel wetting state endowed the Au/C electrode (Au/C-P-0.5) with the best electrochemical CO<sub>2</sub>RR performance and improved CO<sub>2</sub> mass transfer efficiency over the interface even at large current densities.

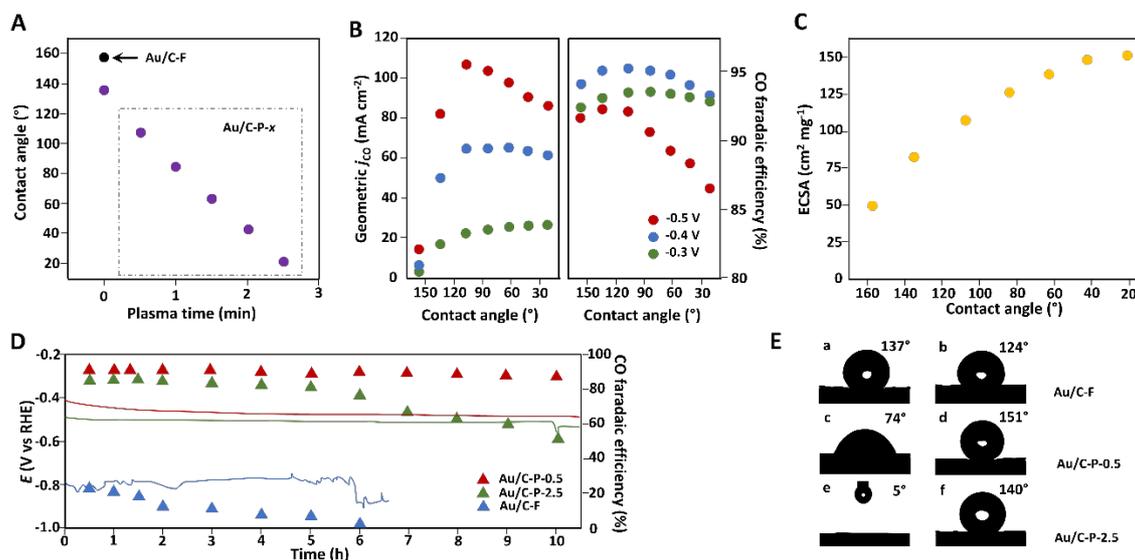
**Picture 1A** shows the fabrication procedure of modified electrodes with different wettability involving superhydrophobicity and hydrophilicity. Polytetrafluoroethylene (PTFE)-modified carbon fiber paper was used as a superhydrophobic porous gas diffusion layer (GDL) with a water contact angle (CA) of  $151 \pm 2^\circ$ . After the deposition of an Au/C NP catalyst layer the CA

decreased to  $135 \pm 3^\circ$ . Notably, scanning electron microscopy results show that the catalyst layer was supported by carbon fibers without penetrating into the pores of the GDL, which greatly contributed to the rapid interfacial  $\text{CO}_2$  transportation through the porous electrode (Picture 1B&C).



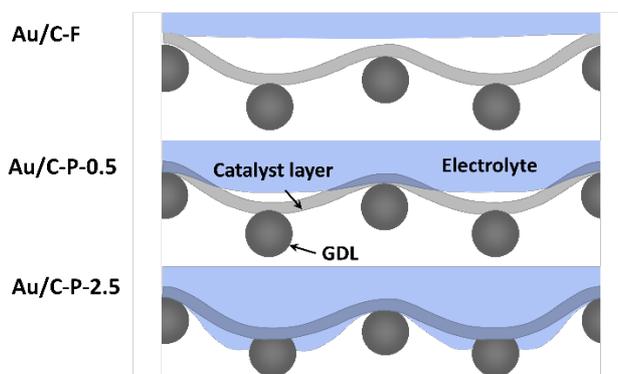
**Picture 1.** (A) Scheme of the electrode preparation and surface modification processes; (B) Illustration of the electrochemical cathode; (C) Gas-liquid-solid interfaces of TPC system.

Two modification methods were applied to induce a range of wettability: fluorine-terminated silane modification (Au/C-F) and plasma treatment (Au/C-P). As shown in **Picture 1A**, the superhydrophobic electrode Au/C-F, the hydrophobic electrode Au/C-P-0.5 and the hydrophilic electrode Au/C-P-2.5 were generated (0.5 and 2.5 denote plasma treatment time in min). A longer plasma treatment time resulted in an increased amount of oxygen-containing functional groups on the electrodes, thus Au/C-P-2.5 was more hydrophilic than Au/C-P-0.5 (**Picture 2A**).



**Picture 2.** (A) CAs against different plasma treatment time. (B) Geometric  $j_{\text{CO}}$  and CO Faradaic efficiency of Au/C electrodes against CAs at different potentials. (C) The electrochemical surface area (ECSA) of Au/C electrodes against CAs. (D) Cathodic potentials and  $\text{CO}_2$ RR stabilities of Au/C electrodes at  $100 \text{ mA cm}^{-2}$ . (E) CAs of the front side (a, c, e) and the reverse side (b, d, f) of Au/C-F, Au/C-P-0.5 and Au/C-P-2.5 after stability tests

To further demonstrate the effect of wettability of the Au/C catalyst layer on both interfacial CO<sub>2</sub> transportation and electrochemical reduction, the authors investigated the electrochemical CO<sub>2</sub>RR performance of different Au/C electrodes in TPC systems. **Picture 2B** clearly shows the wettability dramatically influenced the CO partial current density ( $j_{\text{CO}}$ ) and CO Faradaic efficiency, especially under a large bias potentials. The electrochemical surface area (ECSA) of the Au/C electrodes increases with decreased CAs (more hydrophilic catalyst layer) (**Picture 2C**). Moreover, **Picture 2D** illustrates extremely different cathodic potentials and CO<sub>2</sub>RR stabilities for three typical Au/C electrodes (Au/C-F, Au/C-P-0.5 and Au/C-P-2.5) at high current density (100 mA cm<sup>-2</sup>). The superhydrophobic Au/C-F exhibited a negative potential with very low CO Faradaic efficiency (implying poor contact between catalyst and electrolyte). Also, the CAs on the front side and reverse side of Au/C-F both decreased by more than 20° after above stability test, indicating that the superhydrophobic system was not stable (**Picture 2E**). Au/C-P-0.5 maintained its potential at  $-0.47 \pm 0.02$  V during the whole stability test, and its CO Faradaic efficiency decreased slightly from 91.8% to 87.3% due to the increased hydrophilicity of the front side (74°). Its reverse side could maintain the superhydrophobicity (151°) under the same conditions. For Au/C-P-2.5, CAs of the front side and reverse side decreased to 5° and 140°, respectively, which shows that the partial penetration of electrolyte into the catalyst layer probably blocked the pores and further decreased the CO Faradaic efficiency from 86.0% to 51.0%. All above results demonstrate that Au/C-P-0.5 with a small overpotential and a high CO Faradaic efficiency outperformed the other two electrodes. Therefore, the wettability of the catalyst layer is essential for reducing the CO<sub>2</sub>RR overpotential and improving the CO<sub>2</sub>RR stability when operating at high current densities.



**Picture 3.** Scheme of interfacial structures of three Au/C electrodes (GDL: gas diffusion layer)

Furthermore, they elucidated the mechanism behind the relationship between the electrochemical performance and the wettability-controlled interfacial structures of Au/C electrodes. As shown in **Picture 3**, the Au/C electrodes exhibited three different wetting states due to different gas-liquid-solid interfaces. The electrolyte penetration depth increased with surface hydrophilicity of the electrode. Specifically, Au/C-F mainly showed a typical liquid-gas interface. For Au/C-P-0.5, the hydrophilicity of the catalyst layer helped the electrolyte to penetrate deep into the electrode and contact with the catalyst layer, thus displaying a Cassie-Wenzel coexistence state; for Au/C-P-2.5, the electrolyte completely penetrated into the electrode, showing a Wenzel state. These wetting states greatly contributed to the different electrochemical CO<sub>2</sub>RR performances of the three Au/C

electrodes from **Picture 2D**. In summary, a Cassie-Wenzel coexistence wetting state with a TPC system improved the CO<sub>2</sub> transportation and helped to maintain a stable CO<sub>2</sub> concentration during the electrochemical reaction.

Overall, the authors have shown that wettability-controlled interfacial structures of are important for interfacial CO<sub>2</sub> transportation and CO<sub>2</sub>RR performance of TPC systems. In particular, Au/C-P-0.5 electrodes with Cassie-Wenzel coexistence wetting state presented an ideal structure for CO<sub>2</sub> transport from the gas phase to the Au active sites at high current densities during the CO<sub>2</sub>RR. This work provides a valuable guideline for improving the electrochemical CO<sub>2</sub>RR efficiency by controlling the interfacial wettability of TPC systems which is expected to be transferrable to other gas diffusion electrode systems as well in the future.

[An optical contour analysis system OCA \(DataPhysics Instruments GmbH, Germany\) was used in this research.](#)

For more information, please refer to the following article:

**Efficient wettability-controlled electroreduction of CO<sub>2</sub> to CO at Au/C interfaces**; Run Shi, Jiahao Guo, Xuerui Zhang, Geoffrey I. N. Waterhouse, Lu Shang, Chao Zhou, Lei Jiang & Tierui Zhang, *Nature communications* **2020**, *11*:3028; DOI: 10.1038/s41467-020-16847-9