Plasmonic-Enhanced Carbon Dioxide Photo-Reduction using Collapsible Nano-fingers

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Carbon dioxide (CO_2) is one of the well-known greenhouse gases that cause global warming and sea level rising. The global CO_2 emissions from the burning of fossil fuels for energy and cement production, however, increased significantly in the past and have reached to emit over 34 billion tonnes each year.[1] There are urgent needs to both reduce the CO_2 concentration and find an alternative fuel source. The CO_2 reduction reaction (CO2RR) is a promising method to both satisfy these needs as it converts water and CO_2 into high energy density chemicals such as carbon monoxide, methanol, and ethylene. Nevertheless, it suffers from the high chemical reaction barrier and the competition between hydrogen evolution. Besides, the low selectivity to generate high energy density products due to those products require more electrons and energy to generate[2] as shown in Table 1, which further hinders CO2RR applications.

In this abstract, we proposed using collapsible nano-fingers (Figure 1) to do CO_2 photo-reduction. From our previous studies, compared with a simple gold film substrate the hot spot intensity generated by our nano-fingers at the resonant frequency around 600 nm is 10,000 larger than its incident light intensity.[3] A high -intensity hot spot can generate a great number of electron-hole pairs inside the TiO_2 spacer that can facilitate the chemical reduction and oxidation reaction. The high-intensity hot spot and tremendous electron-hole pairs would provide additional energy to overcome the chemical reaction barrier as well as provide more electrons to generate high-energy density chemicals.

An isolated cell made by Poly(methyl methacrylate) (PMMA), which only absorbs limited visible light energy, was used to do the experiments; the cell equips with four poles to allow CO_2 gas flows in and out and to collect liquid samples after the experiment (Figure 2a). A 99.999% CO_2 aluminum gas cylinder (Figure 2b) was used to eliminate possible carbon contaminations from the rust in cylinders. A 30-minute CO_2 purging with 0.1 lpm (litter per minute) flow rate into the deionized (DI) water forms CO_2-saturated DI water. After 638 nm, 300 mW, 4 hours laser illumination, we found that higher hydrocarbons were generated in the CO_2-saturated deionized water when nano-fingers existing via the cryogenic NMR measurement while there were no higher hydrocarbons generated with the gold film sample (Figure 3). To our knowledge, this is the first time that chemical reaction pathways are controlled by plasmon.

Product	Chemical Formula	Carbons	Electrons
Carbon Monoxide	CO	C_1	2
Formate	$HCOO^-$	C_1	2
Methane	CH_4	C_1	8
Glycolaldehyde	$C_2H_4O_2$	C_2	8
Acetaldehyde	C_2H_4O	C_2	10
Ethanol	C_2H_6O	C_2	12
Ethylene	C_2H_4	C_2	12
Ethane	C_2H_6	C_2	14
Hydroxyacetone	$C_3H_6O_2$	C_3	14
Acetone	C_3H_6O	C_3	16
Ally Alcohol	C_3H_6O	C_3	16
Propionaldehyde	C_3H_6O	C_3	16
n-Propanol	C_3H_8O	C_3	18

Table 1, 13 products of CO_2 reduction reaction.

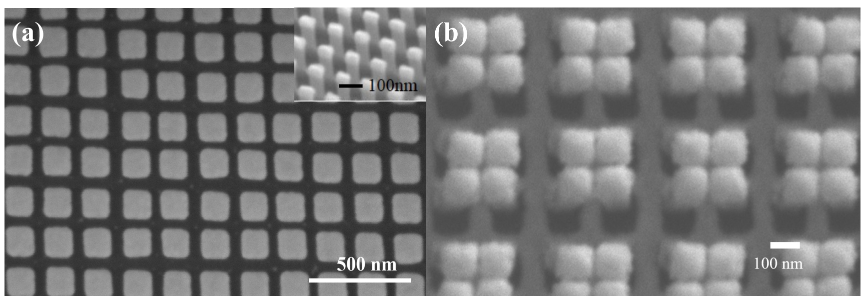

Figure 1, The SEM images of nano-fingers (a) before and (b) after collapsing.

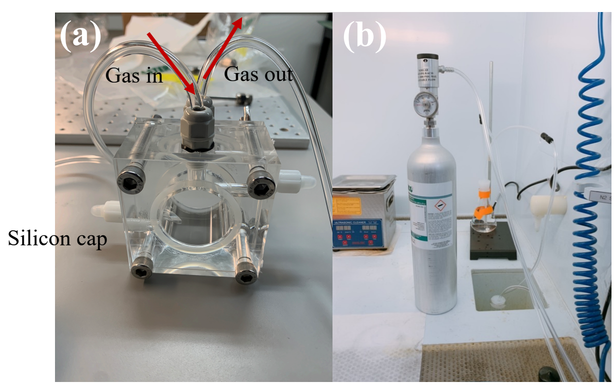

Figure 2, The experiment setup (a) the reaction cell and (b) a 99.999% CO_2 aluminum gas cylinder.

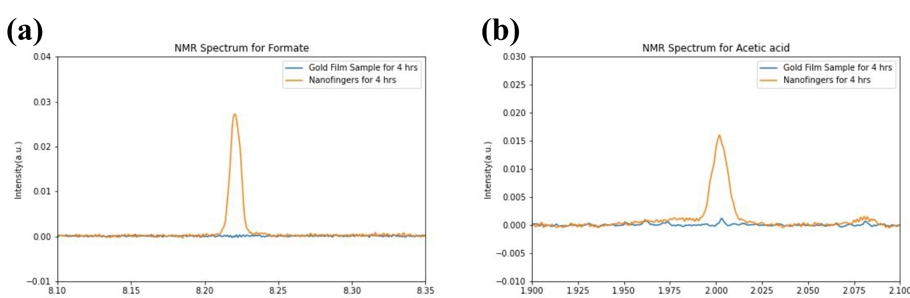

Figure 3, The NMR spectra of (a) Formate and (b) Acetic acid with and without nano-fingers present.

[1] https://ourworldindata.org/co2-emissions
[2] Erin B. Creel, Elizabeth R. Corson, Johanna Eichhorn, Robert Kostecki, Jeffrey J. Urban, and Bryan D. McCloskey, Directing Selectivity of Electrochemical Carbon Dioxide Reduction Using Plasmonics, *ACS Energy Lett.* 2019, 4, 5, 1098–1105
[3] Boxiang Song, Yuhan Yao, Roelof E. Groenewald, Yunxiang Wang, He Liu, Yifei Wang, Yuanrui Li, Fanxin Liu, Stephen B. Cronin, Adam M. Schwartzberg, Stephan Haas, and Wei Wu, Probing Gap Plasmons Down to Subnanometer Scales Using Collapsible Nanofingers, ACS Nano 2017, 11, 5836−5843