Electronic Supplementary Information for

Reduction of CO_2 to Low Carbon Alcohols on CuO FCs/Fe_2O_3 NTs Catalyst with Photoelectric Dual Catalytic Interfaces

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Figure S1. The current transient during anodization of Fe in an 0.25 wt.% NH_4F non-aqueous solution (Volume of water : glycol = 3:97) at 30 V.

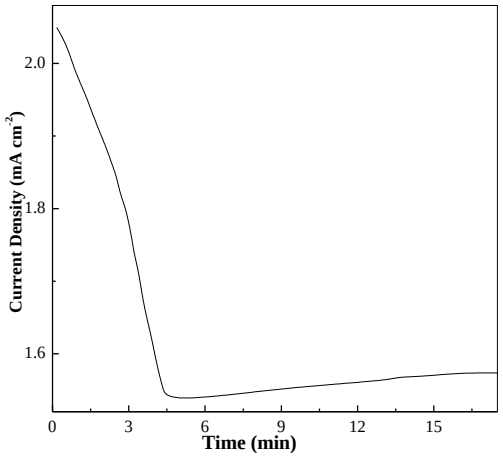
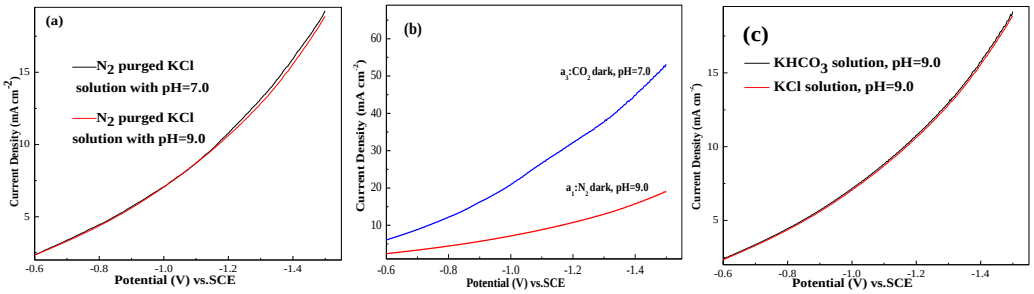


Figure. S2a Electrocatalytic protons reduction of CuO FCs/Fe_2O_3 NTs in 0.1 mol L^{-1} KCl solution with different pH.

Figure. S2b Electrocatalytic CO_2 reduction of CuO FCs/Fe_2O_3 NTs in 0.1 mol L^{-1} $KHCO_3$ solution.

Figure. S2c Electrocatalytic performance of CuO FCs/Fe_2O_3 NTs in different solutions with the same pH of 9.0 (0.1mol L^{-1} KCl solution with the assistance of 0.1mol L^{-1} KOH solution and 0.1mol L^{-1} $KHCO_3$ solution, both purged with nitrogen).



(1) The effect of proton reduction

The KCl solution with pH = 7.0 and pH = 9.0 were prepared with the assistance of 0.1mol L^{-1} HCl and 0.1mol L^{-1} KOH solution, respectively. The difference of reduction current density (Figure S4a) was caused purely by the different proton reduction rate.

The different current density in Figure S4b must be caused by both proton reduction and CO_2 reduction.

We calculated the ratio of protons reduction is 0.12%. The equation was as followed:

$$\begin{aligned} \text{ratio}_{\text{proton reduction(-1.1V)}} &= \frac{\text{proton reduction}}{\text{proton reduction} + \text{co}_2 \text{ reduction}} \times 100\% \\ &= \frac{\text{current density}_{\text{KCl}_{\text{pH7}}} - \text{current density}_{\text{KCl}_{\text{pH9}}}}{\text{current density}_{\text{KHCO}_{3(\text{pH7})}} - \text{current density}_{\text{KHCO}_{3(\text{pH9})}}} \times 100\% \\ &= \frac{8.7354 - 8.7143}{26.6171 - 8.8170} \times 100\% \\ &= 0.12\% \end{aligned} \quad (1)$$

So we could think that the protons reduction has no impact on our experimental conclusion.

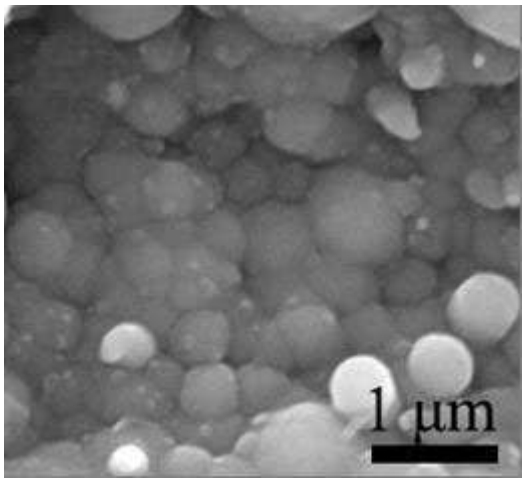
(2) The effect of CO_2 reduction in bicarbonate solution itself

It must be no reduction of CO_2 in the as mentioned above KCl solution. So the comparison between the two solutions (Figure S4c) can explain the small CO_2 reduction in bicarbonate solution itself. The proportion of CO_2 reduction in bicarbonate solution itself can be calculated by the following equation:

$$\begin{aligned} \text{ratio}_{CO_2 \text{ reduction in bicarbonate itself (-1.1V)}} &= \frac{\text{current density}_{KHCO_{3(pH9)}} - \text{current density}_{KCl_{pH9}}}{\text{current density}_{KHCO_{3(pH7)}} - \text{current density}_{KHCO_{3(pH9)}}} \times 100\% \\ &= \frac{8.8170 - 8.7143}{26.6171 - 8.8170} \times 100\% \\ &= 0.58\% \end{aligned} \quad (2)$$

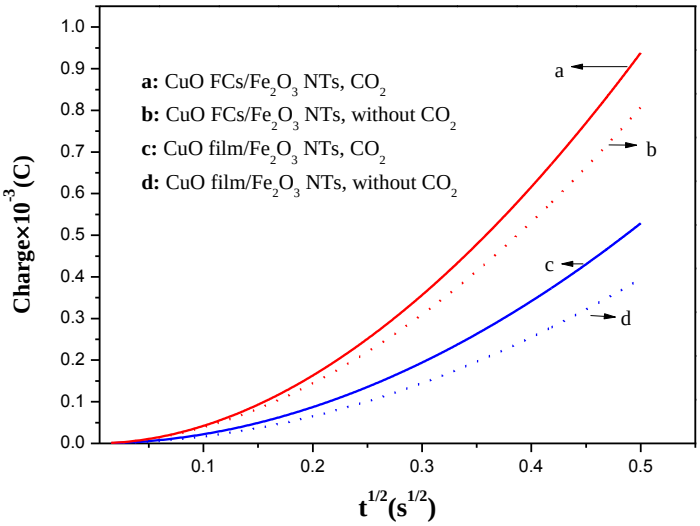
The ratio (0.58%) of CO_2 reduction in bicarbonate solution itself fully explained the following two points of view: 1) In bicarbonate solutions, even with nitrogen purge, there could be a small CO_2 reduction. 2) The small CO_2 reduction in bicarbonate solution itself has no impact on our conclusion.

Figure S3. The SEM image of the CuO film/Fe_2O_3 NTs



The Fe_2O_3 NTs prepared method is the same as CuO FCs/Fe_2O_3 NTs. And the CuO film/Fe_2O_3 NTs was prepared by potentiostatic method, the detailed prepared condition as followed: the electrolyte 0.4 M $CuSO_4$ + 3 M lactic acid; constant potential 0.5 V; pH = 8.0; deposition temperature 50 ^oC; deposition time 15 minutes.

Figure S4. Chronocoulometry curves on CuO FCs/Fe_2O_3 NTs and CuO film/Fe_2O_3 NTs

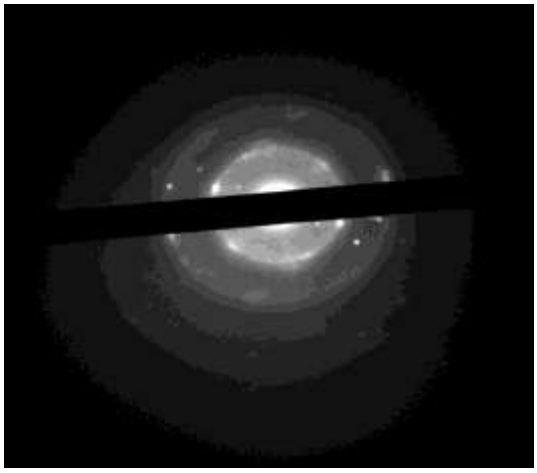


The adsorptive active site volume G calculated method was listed below: According to the Cottrell theory: $Q=nFG+Q_{d1}+2nFAC^0_{ox}D^{1/2}t^{1/2}/\Pi^{1/2}$, it can be seen from the formula that the total charge Q has a linear relationship with the $t^{1/2}$, but also the intercept in charge-axis is $nFG+Q_{dl}$, in the blank medium sulfate solution that the intercept is measured as Q_{dl}, the difference is nFG, thus the reaction volume G in the electrode surface can be obtained (n=1). The electrochemical adsoptive amount for the CO_2 on the CuO FCs/Fe_2O_3 NTs and CuO film/Fe_2O_3 NTs is 1.65 nmol and 0.62 nmol, respectively. The former is 2.66 times of the later.

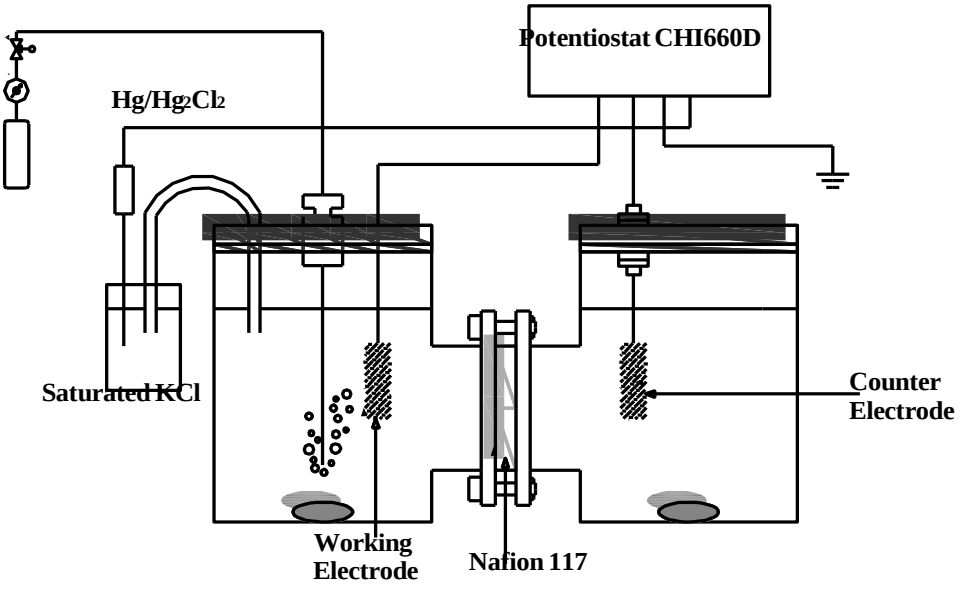
Table S1. Comparison between CuO FCs/Fe_2O_3 NTs and CuO film/Fe_2O_3 NTs

	CuO FCs/Fe_2O_3 NTs	CuO film/Fe_2O_3 NTs
Methanol	FE 91.20%	FE 15.11%
	PS 81.80%	PS 47.06%
Ethanol	FE 9.80%	0
	PS 8.80%	0
Methane	FE 10.46%	FE 24.92%
	PS 9.40%	PS 52.94%
CO_2 conversiton (%)	16.92%	3.03%

Figure S5. The SAED parten of CuO FCs/Fe_2O_3NTs



191 **Figure S6**. The experimental device of photoelectrocatalytic properties



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