Support Information

The Construction of p/n-Cu_2O Heterojunction Catalysts for Efficient CO_2 Photoelectric Reduction

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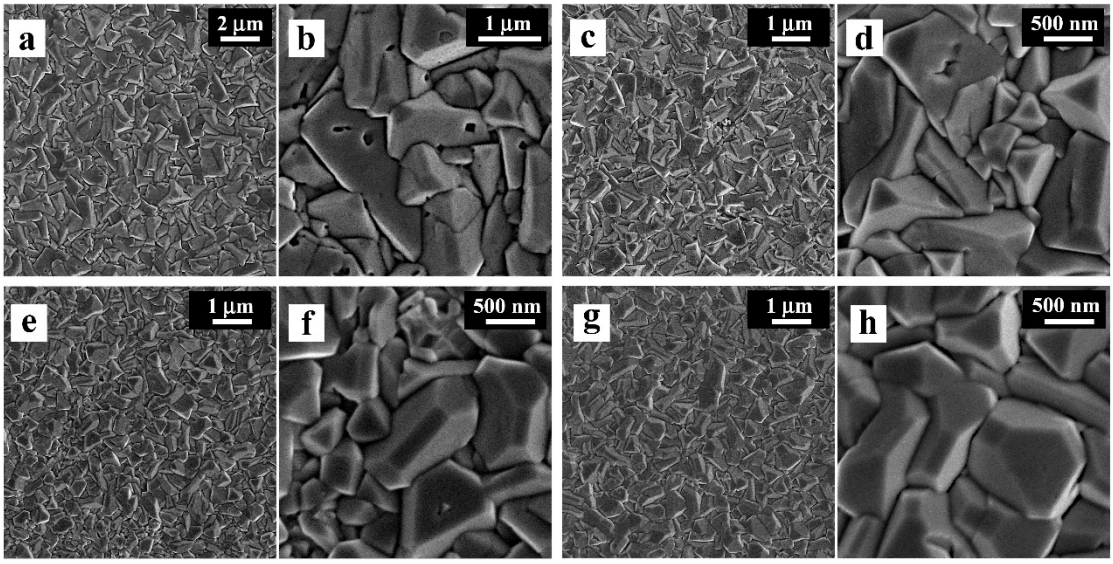

Figure S1. The top view SEM images of (a) p-0.5mAh/n-0.02mAh Cu_2O, (b) p-0.5mAh/n-0.03mAh Cu_2O, (c) p-0.5mAh/n-0.04mAh Cu_2O, (d) p-0.5mAh/n-0.05mAh Cu_2O.

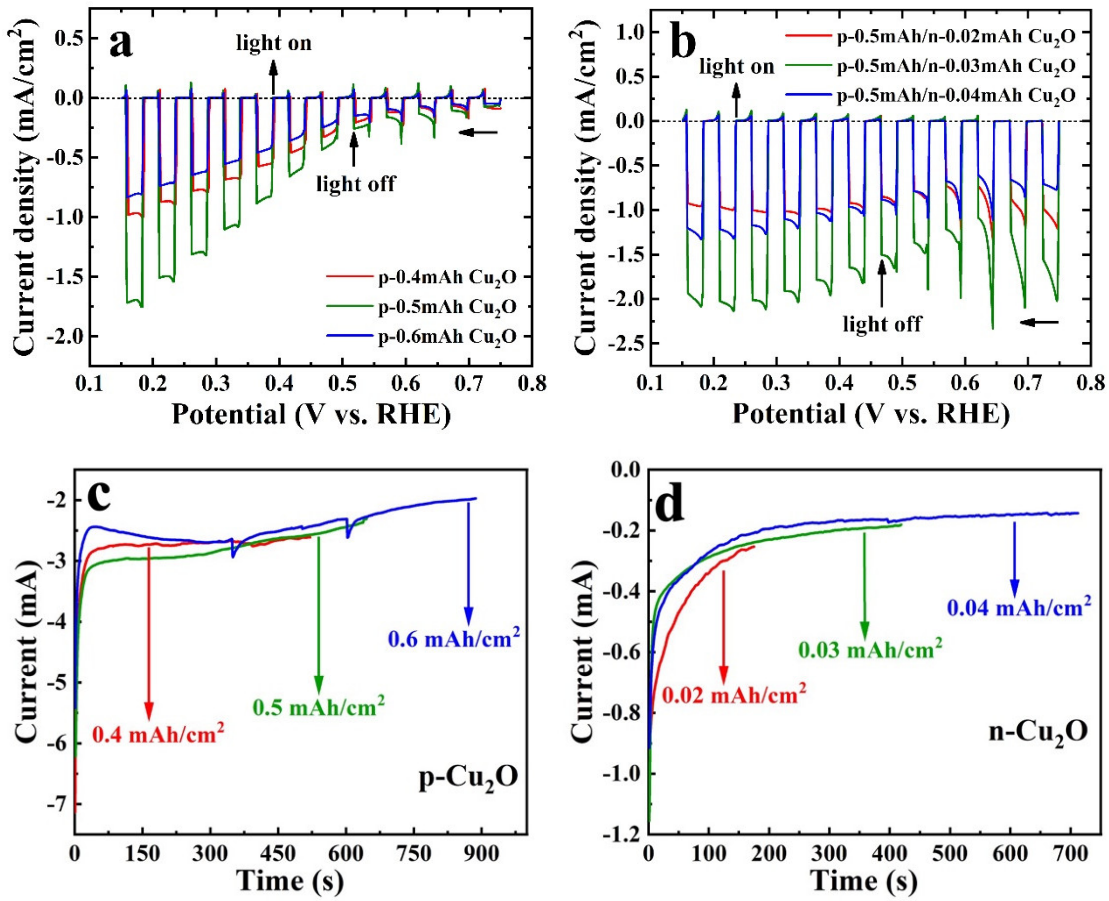

Figure S2. (**a**) LSV curves of p-Cu_2O with different amounts of deposited charge, the electrolyte: (0.1 mol/L $NaHCO_3$); (**b**) LSV curves of n-Cu_2O with different quantities of deposited charge, the electrolyte: (0.1 mol/L $NaHCO_3$); (**c**) Time-current curves of p-Cu_2O with different amounts of deposited charge; (**d**) Time-current curves of n-Cu_2O with varying quantities of deposited charge, substrate: p-Cu_2O (0.5 mAh/cm^2).

Since the 0.1 mol/L $NaHCO_3$ solution is easy to prepare and inexpensive, we used this solution to select our optimal sample for further investigation. The active size of the sample is 1 cm^2. Comparing the photocurrent density of p-Cu_2O samples when the deposited charge was 0.4 mAh/cm^2, 0.5 mAh/cm^2 and 0.6 mAh/cm^2, we found that when the deposited charge was 0.5 mAh/cm^2, the photocurrent density of p-Cu_2O samples was the most significant. The performance was optimal, and too much or too little deposition would affect its performance. Using the same method, p-Cu_2O(0.5 mAh/cm^2) was selected as the substrate, and we compared the photocurrent density of n-Cu_2O when the deposition charge was 0.02 mAh/cm^2, 0.03 mAh/cm^2, and 0.04 mAh/cm^2. We found that when the deposition charge was 0.03 mAh/cm^2, the photocurrent density of p/n-Cu_2O samples was the largest, the performance was the best, and too much or too little deposition would affect its performance. Therefore, we believe that p/n-Cu_2O has the best performance when the deposition charge of p-Cu_2O is 0.5 mAh/cm^2 and the deposition charge of n-Cu_2O is 0.03 mAh/cm^2. Electrochemical reactions generate the photocurrent, and CO_2 reduction is a crucial electrochemical behavior for generating a photocurrent. Through qualitative analysis, we believe that the sample with the highest photocurrent density has the best CO_2 reduction performance. Therefore, we conducted a series of test studies on the selected samples in this study.

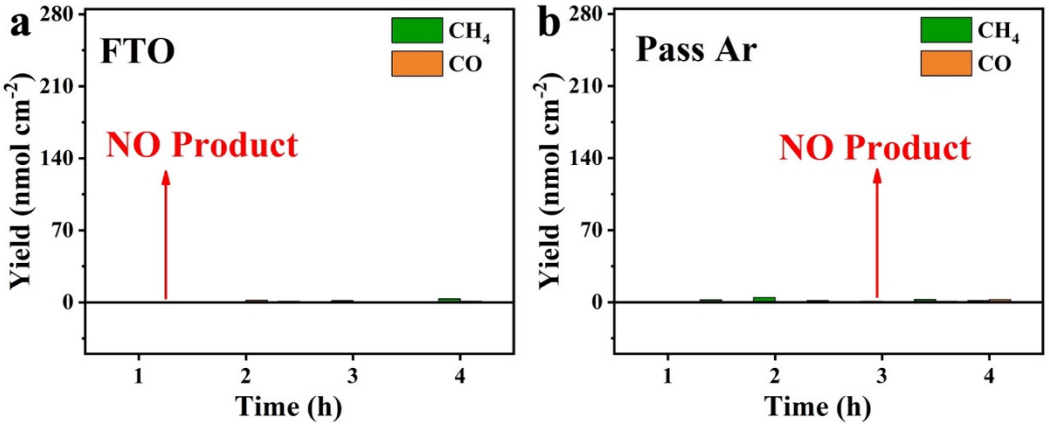

Figure S3. (a) CO_2 reduction yield (0.1 mol/L $C_6H_{15}NO_3/CH_3CN$ + 0.1 mol/L $C_{16}H_{36}F_6NP/CH_3CN$, pH = 9.3, the sample is FTO); (b) CO_2 reduction yield (0.1 mol/L $C_6H_{15}NO_3/CH_3CN$ + 0.1 mol/L $C_{16}H_{36}F_6NP/CH_3CN$, pH = 9.3, pass Ar).

We designed two experiments: (1) Take the FTO as the sample for testing, and the rest of the test conditions remain unchanged; (2) Replace the CO_2 gas introduced before the reaction with Ar gas, and the rest of the test conditions remain unchanged. The test

results showed that when replacing p/n-Cu_2O with FTO, only trace impurity gases were present, and no product was produced. Similarly, when replacing CO_2 with Ar, only trace impurity gases are present, and no products are manufactured. Therefore, we believe that CO_2 reduction rather than other pollutants produces CO and CH_4.

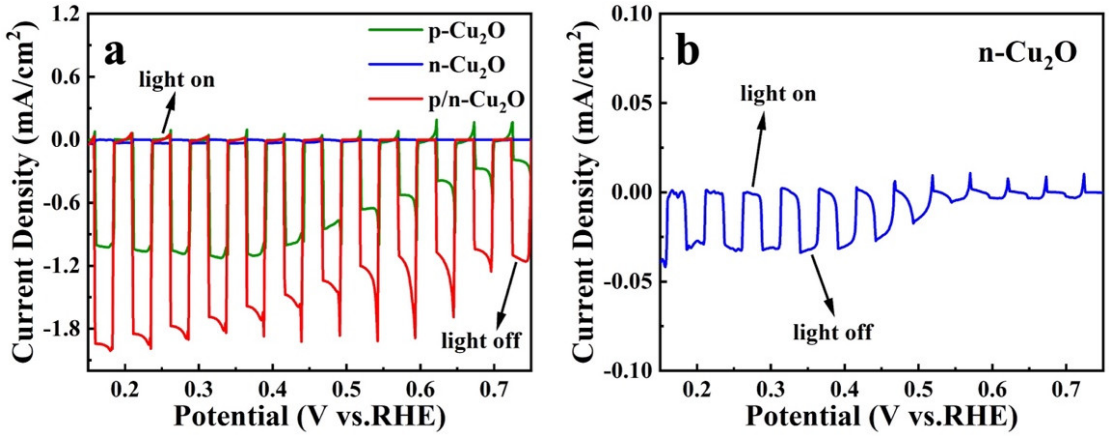

Figure S4. (**a**) LSV of p-Cu_2O, n-Cu_2O, p/n-Cu_2O; (**b**) LSV of n-Cu_2O. The electrolyte: (0.1 mol/L $NaHCO_3$), the deposited charge: (p-Cu_2O: 0.5 mAh/cm^2, n-Cu_2O: 0.03 mAh/cm^2).

As can be seen from Figure S4, the photocurrent density of n-Cu_2O is very low compared to p-Cu_2O and p/n-Cu_2O. The primary function of n-Cu_2O is to promote the separation of photogenerated carriers by constructing a heterojunction with p-Cu_2O, thereby improving the reduction efficiency of CO_2.

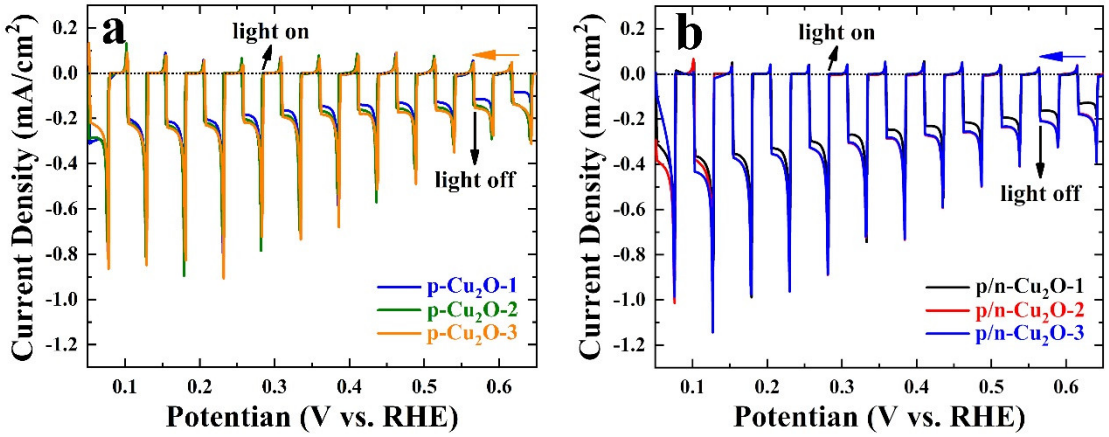

Figure S5. LSV curves of multiple samples of (**a**) p-Cu_2O (p-0.5mAh Cu_2O). LSV curves of multiple samples of (**b**) p/n-Cu_2O (p-0.5mAh/n-0.03mAh Cu_2O).

Figure S5 (a) (b) shows the LSV tests of the multiple samples of p-Cu_2O (p-0.5mAh Cu_2O) and p/n-Cu_2O (p-0.5mAh/n-0.03mAh Cu_2O), respectively. The performance of p-Cu_2O and p/n-Cu_2O samples is stable and repeatable.