Supplementary Materials for

CuO Nanoparticle Supported on TiO_2 with High Efficiency for CO_2 Electrochemical Reduction to Ethanol

Jing Yuan, Jing-Jie Zhang, Man-Ping Yang, Wang-Jun Meng, Huan Wang* and Jia-Xing Lu**

Supplementary Tables and Figures

1. ICP analysis of various CuO/TiO_2 catalysts

Table S1. CuO composition of the synthesized CuO/TiO_2 catalysts

Catalysts	CuO loading (wt%)	
	Intended	Actual[a]
CuO/TiO_2-1	5	4.29
CuO/TiO_2-2	10	8.91
CuO/TiO_2-3	20	18.47
CuO/TiO_2-4	40	36.98
CuO/TiO_2-5	60	51.64
CuO/TiO_2-6	80	74.21

[a] Obtained by ICP

2. High-resolution XPS spectrum of C 1s for CuO/TiO_2-5 catalyst

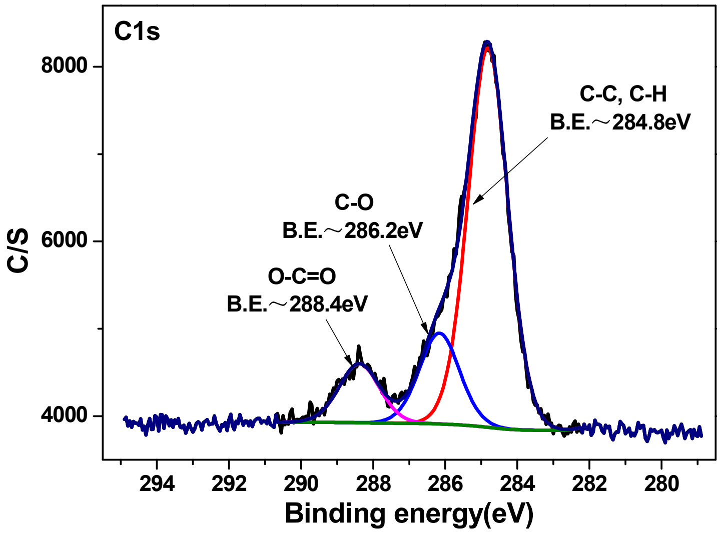


Figure S1. The high-resolution XPS spectrum of C1s for CuO/TiO_2-5 catalyst.

Figure S1 shows the high resolution spectrum of C1s. The binding energy at 284.8, 286.2 and 288.4 eV of C1s are consistent with C-C or C-H, C-O and O-C=O respectively. [1]

3. SEM images of various CuO/TiO_2 catalysts

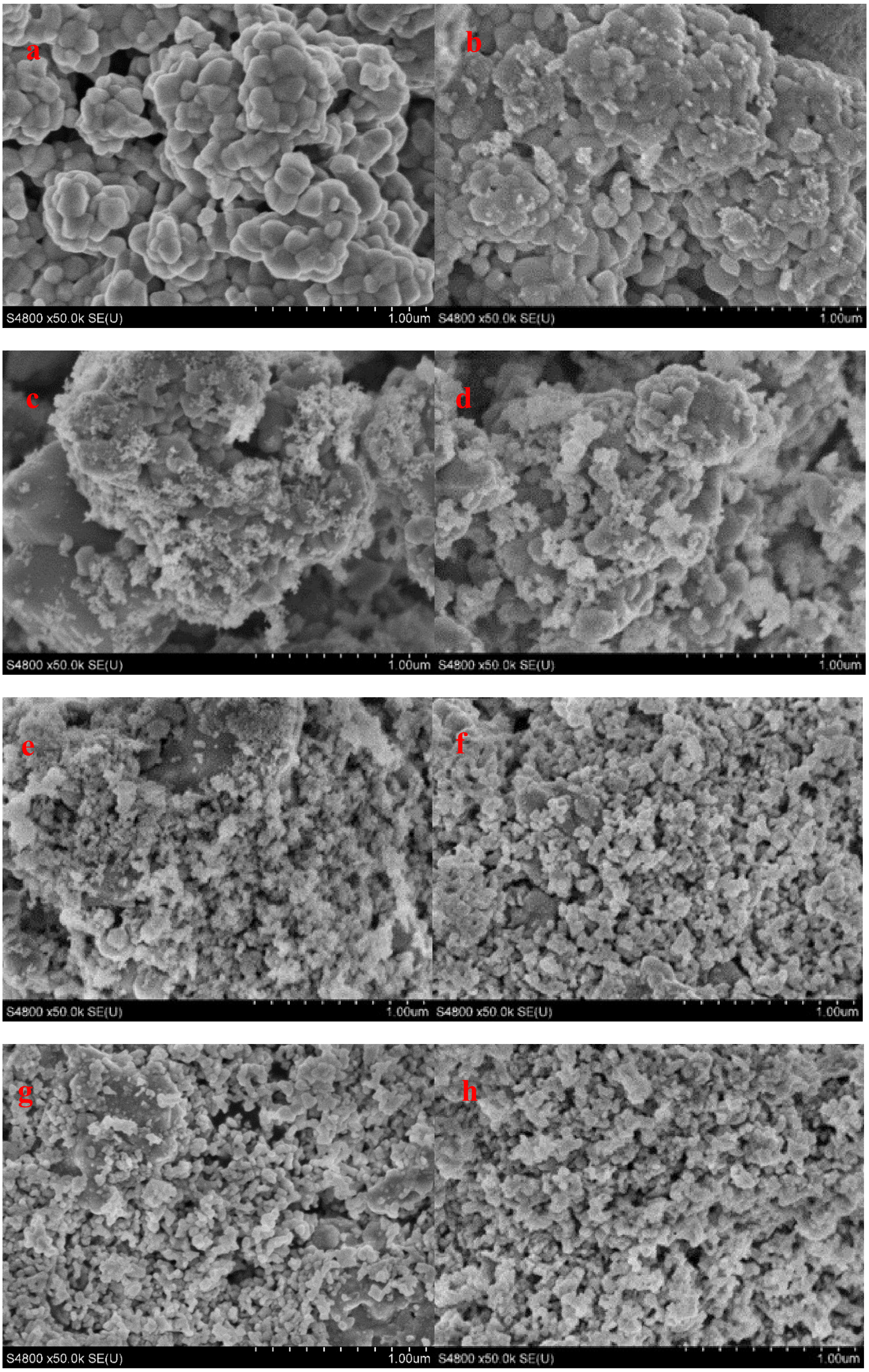


Figure S2. SEM images of: (a) pure TiO_2; (b) CuO/TiO_2-1; (c) CuO/TiO_2-2; (d) CuO/TiO_2-3; (e) CuO/TiO_2-4; (f) CuO/TiO_2-5; (g) CuO/TiO_2-6 and (h) pure CuO.

4. XRD of CuO/TiO_2-5 catalyst after 2 h electrolysis

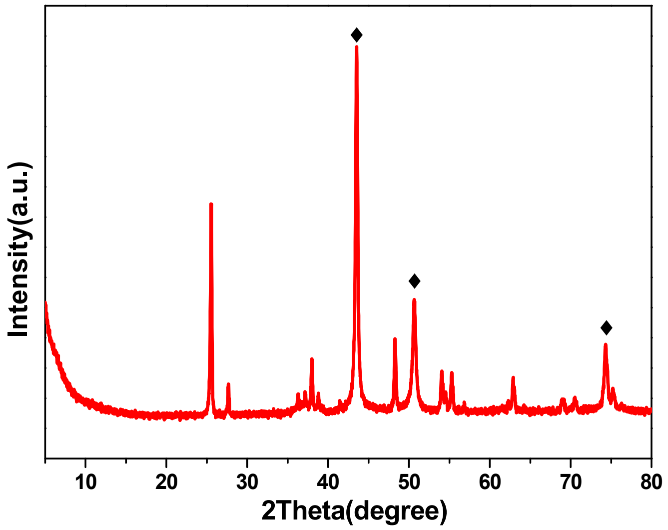


Figure S3. XRD patterns of CuO/TiO_2-5 catalyst after 2h electrolysis. The solid diamond represents the in situ generated Cu metal.

5. Electrolysis test of CuO/TiO_2-5

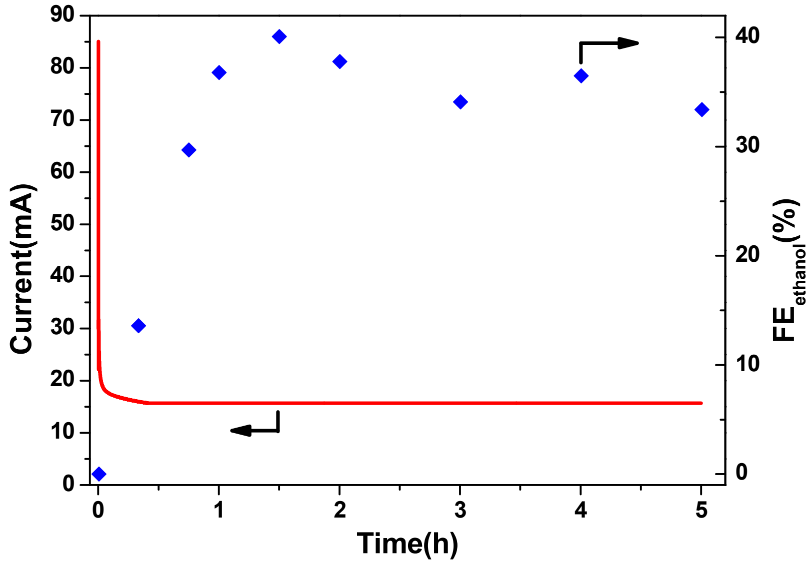


Figure S4. Long-term stability of CuO/TiO_2-5 for CO_2 electroreduction at -0.85 V vs. RHE for 5 h.

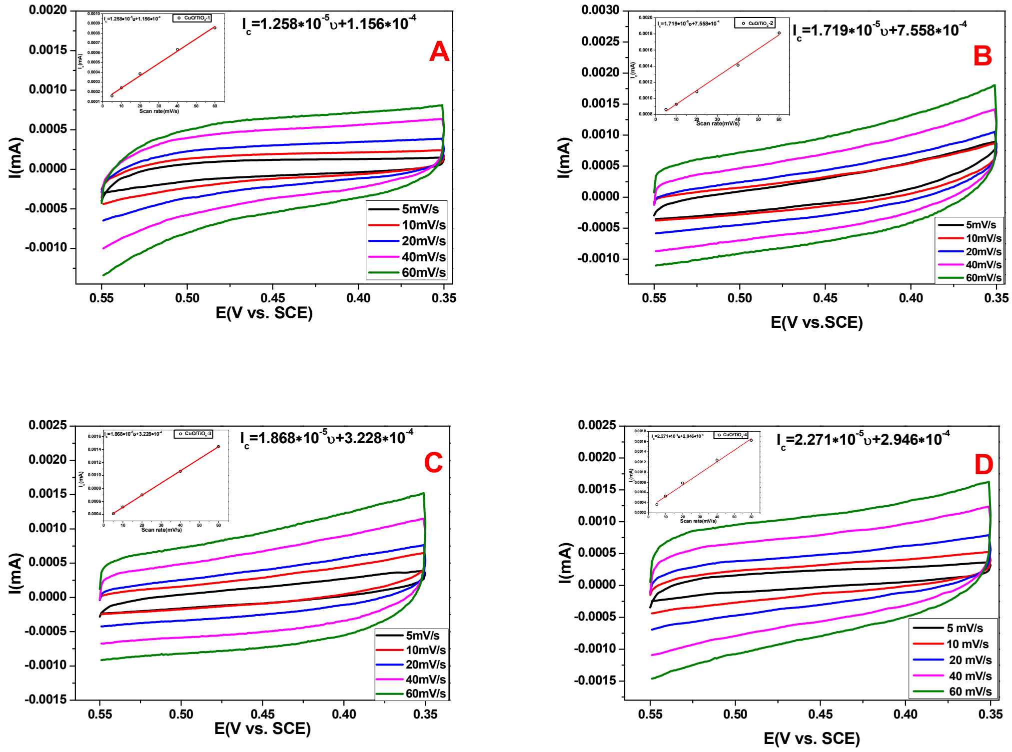
6. The summary of various CuO/TiO_2 catalysts for electrochemical performance

Table S2. The current density (J) for all the CuO/TiO_2 catalysts in CO_2-saturated environment at the potential of -0.85 V vs. RHE.

Entry	**Samples**	**J (mA/cm^2)**
1	CuO/TiO_2-1	1.69
2	CuO/TiO_2-2	2.03
3	CuO/TiO_2-3	3.42
4	CuO/TiO_2-4	6.35
5	CuO/TiO_2-5	8.25
6	CuO/TiO_2-6	6.97
7	Pure CuO	5.95

7. Electrochemistry surface area (ECSA)

To examine the active surface of the working electrode with coated CuO/TiO_2 catalysts, the double layer capacitance in N_2-saturated 0.1 M $HClO_4$ solution was measured by CV in a potential range without faradaic process occurred. The scan rates (ν) were 5 mV/s, 10 mV/s, 20 mV/s, 40 mV/s and 60 mV/s, respectively. The double layer capacitance (C_{dl}) was calculated by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of CV stripping using the straight line inset in **Figure S5**. ECSA was estimated from the ratio of C_{dl} for the working electrode and the corresponding pure metal oxide CuO electrode (C_s). Due to the same C_s, ECSA for CuO/TiO_2 catalysts are positive correlation with C_{dl}. Additionally, the C_{dl} was assessed by plotting the cathodic current (I_c) at 0.45 V vs. SCE against the scan rate ($C_{dl}=I_c/\nu$). As shown in **Figure S5**, CV curves are recorded for various CuO/TiO_2 and CuO/C samples, different samples exhibit different C_{dl} (summarized in **Table S3**).



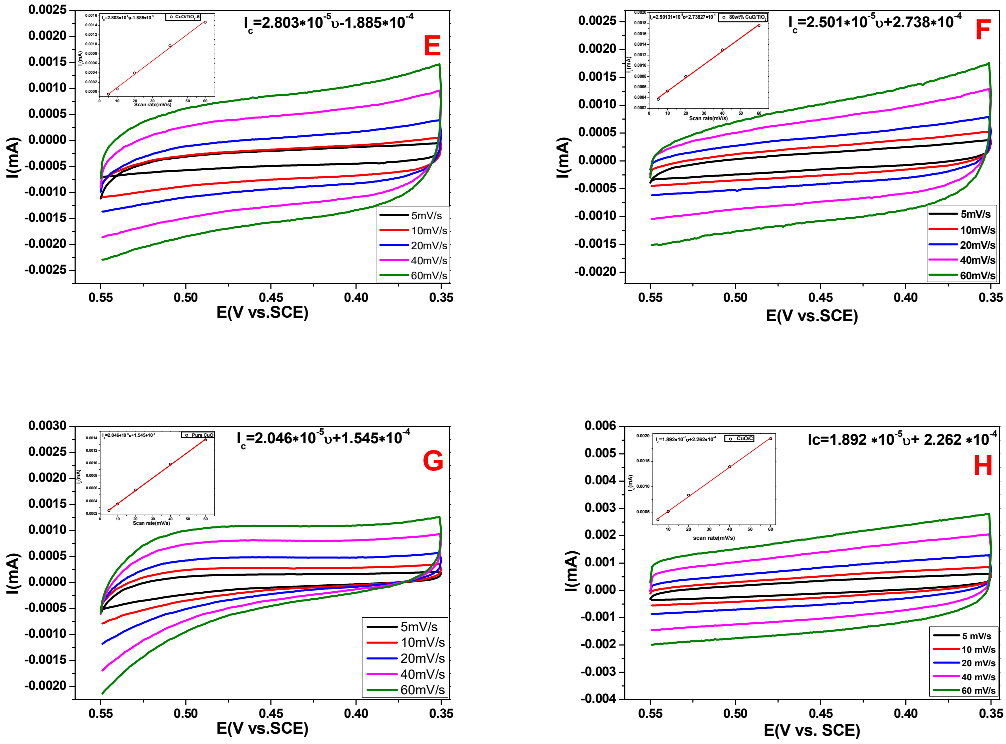


Figure S5. Plot of I vs potential of (A) CuO/TiO_2-1; (B) CuO/TiO_2-2; (C) CuO/TiO_2-3; (D) CuO/TiO_2-4; (E) CuO/TiO_2-5; (F) CuO/TiO_2-6; (G) pure CuO; and (H) CuO/C in N_2-saturated 0.1M $HClO_4$ solution cycled between 0.35 and 0.55 V vs. SCE at scan rates in the range of 5-60 mV/s. Insets show plot of I_c vs ν where the linear regressions give capacitance information.

Table S3. The analysis of C_{dl} of various CuO/TiO_2 and CuO/C catalysts

Entry	Catalyst	C_{dl} (μF)
1	CuO/TiO_2-1	12.58
2	CuO/TiO_2-2	17.19
3	CuO/TiO_2-3	18.69
4	CuO/TiO_2-4	22.71
5	CuO/TiO_2-5	28.03
6	CuO/TiO_2-6	25.01
7	Pure CuO	20.46
8	CuO/C	18.93

8. The analysis of specific surface area of CuO/TiO_2 catalysts

Table S4. The analysis of specific surface area of CuO/TiO_2 catalysts

Material	Surface area (m^2/g)[a]
TiO_2	3.75
CuO/TiO_2-1	6.41
CuO/TiO_2-2	8.42
CuO/TiO_2-3	8.91
CuO/TiO_2-4	16.12
CuO/TiO_2-5	21.77
CuO/TiO_2-6	18.25
CuO	14.34
CuO/C	9.43

[a] Obtained by BET

9. Material characterization pattern of CuO/C and C

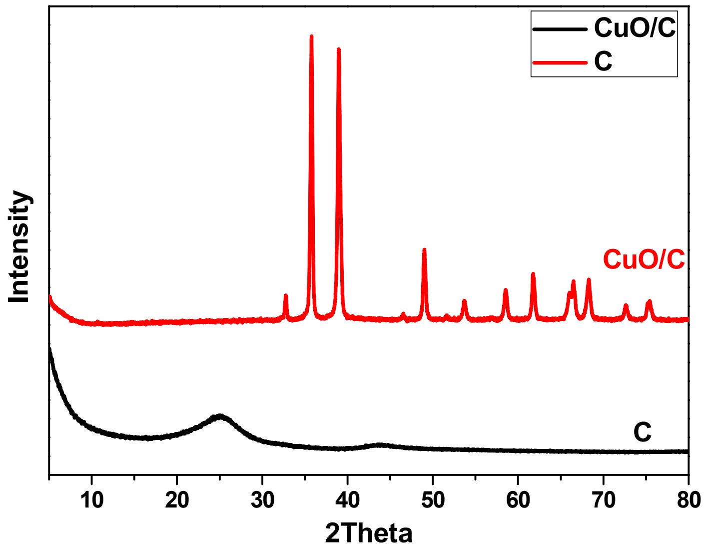


Figure S6. XRD patterns of CuO/C and C catalysts.

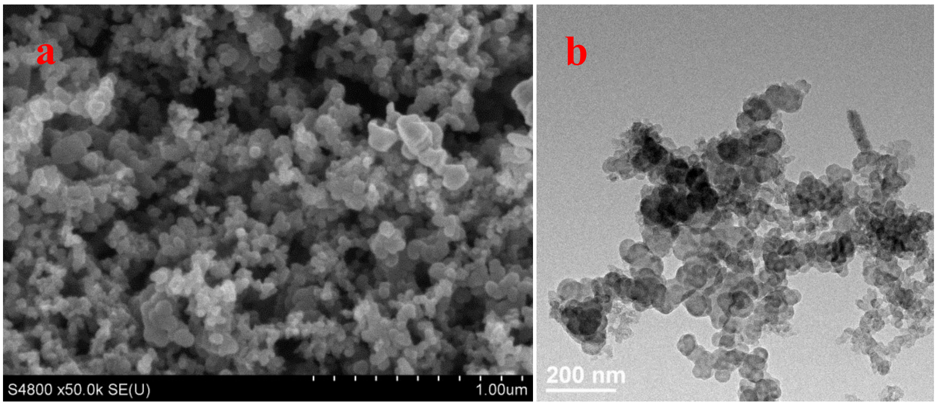


Figure S7. SEM (a) and TEM (b) images of CuO/C catalyst.

10. Electrochemical characterization of CuO/C

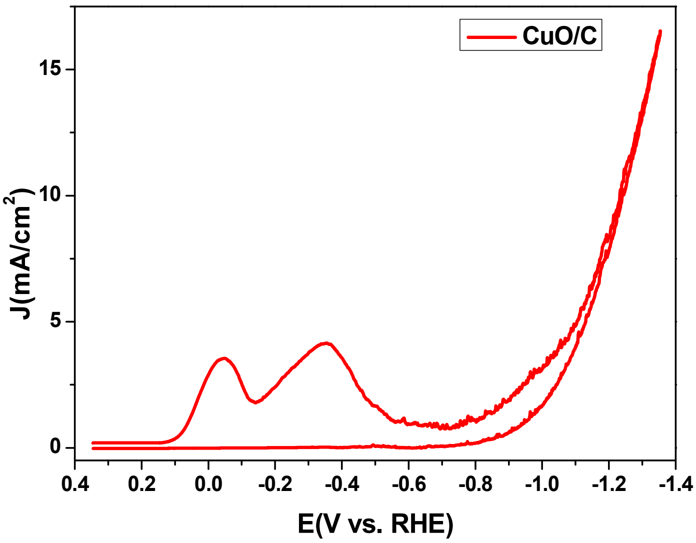


Figure S8. CV curve of CuO/C catalyst over glassy carbon electrode in CO_2-saturated (red line) 0.5 M $KHCO_3$ solution.

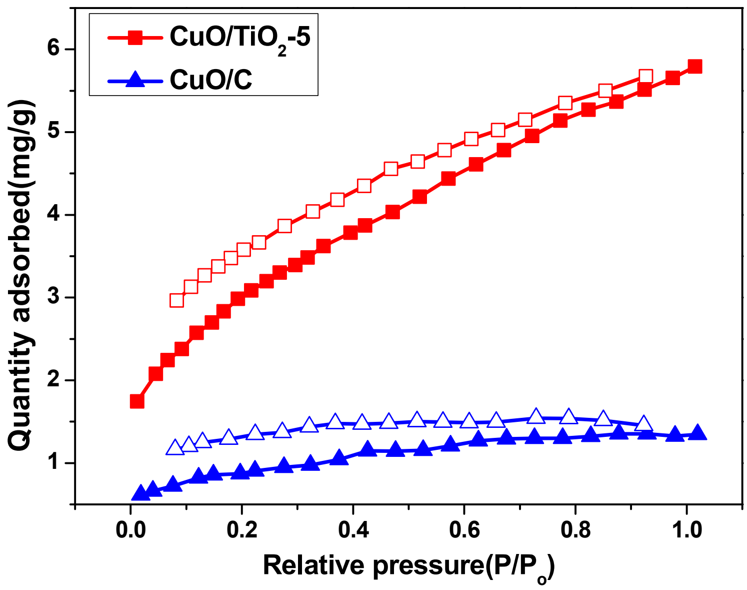


Figure S9. CO_2 adsorption-desorption isotherms at 297K of CuO/TiO_2-5 (red square) and CuO/C (blue triangle), Filled and empty symbols represent adsorption and desorption, respectively.

Reference

1. Bai, L.; Qiao, S.; Fang, Y.; Tian, J.; Mcleod, J.; Song,Y.; Huang, H.; Liu, Y.; Kang, Z. Third-order nonlinear optical properties of carboxyl group dominant carbon nanodots. *J. Mater. Chem. C* **2016**, *4*, 8490-8495.