

## Controlled synthesis of $\text{Bi}_2\text{O}_3\text{-CuO}$ catalysis for selective electrochemical reduction of $\text{CO}_2$ to formate

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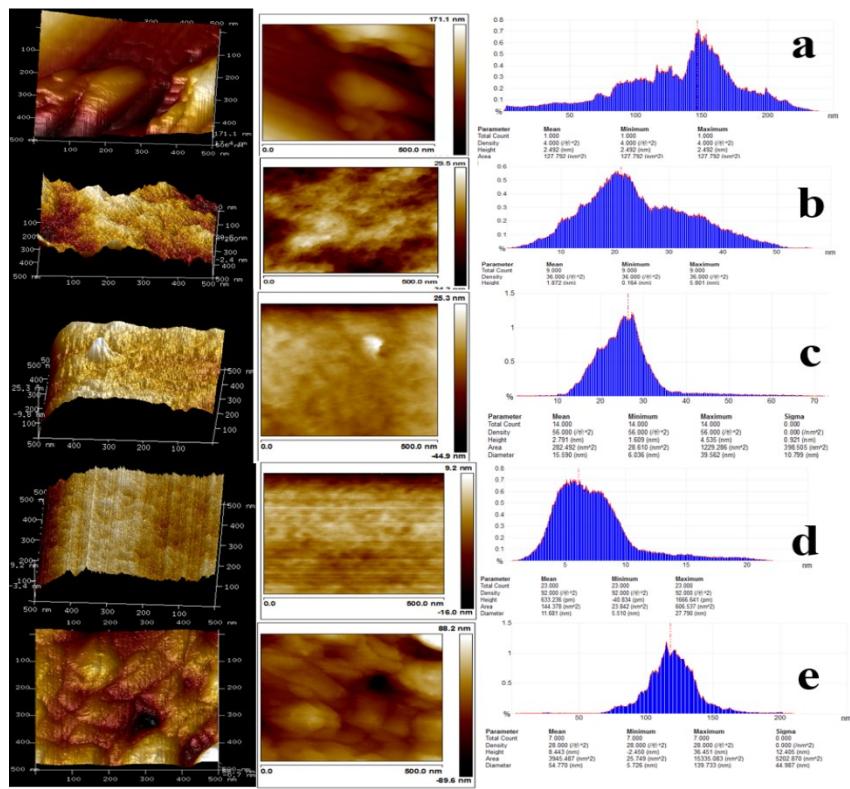
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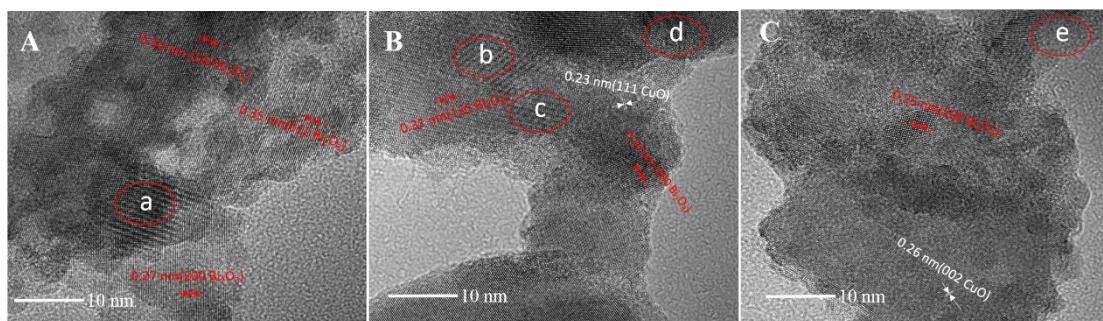
## SUPPLEMENTARY MATERIAL



**Fig S 1.** AFM images before and after catalytic reduction of  $\text{Bi}_2\text{O}_3\text{-CuO}(x)$  catalysts: (a,  $x=0.5$ ; b,  $x=0.5$  (reduction); c,  $x=0.75$ ; d,  $x=0.75$  (reduction)); e,  $x=1.0$ )

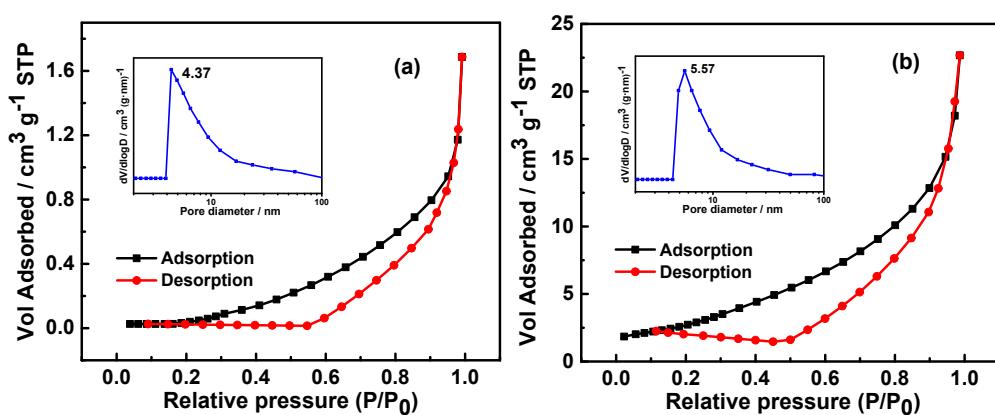
**Table S 1.** The particle size distribution before and after electroreduction of  $\text{Bi}_2\text{O}_3\text{-CuO}(x)$  catalysts ( $x=0.5, 0.75, 1.0$ ) were obtained by AFM analysis

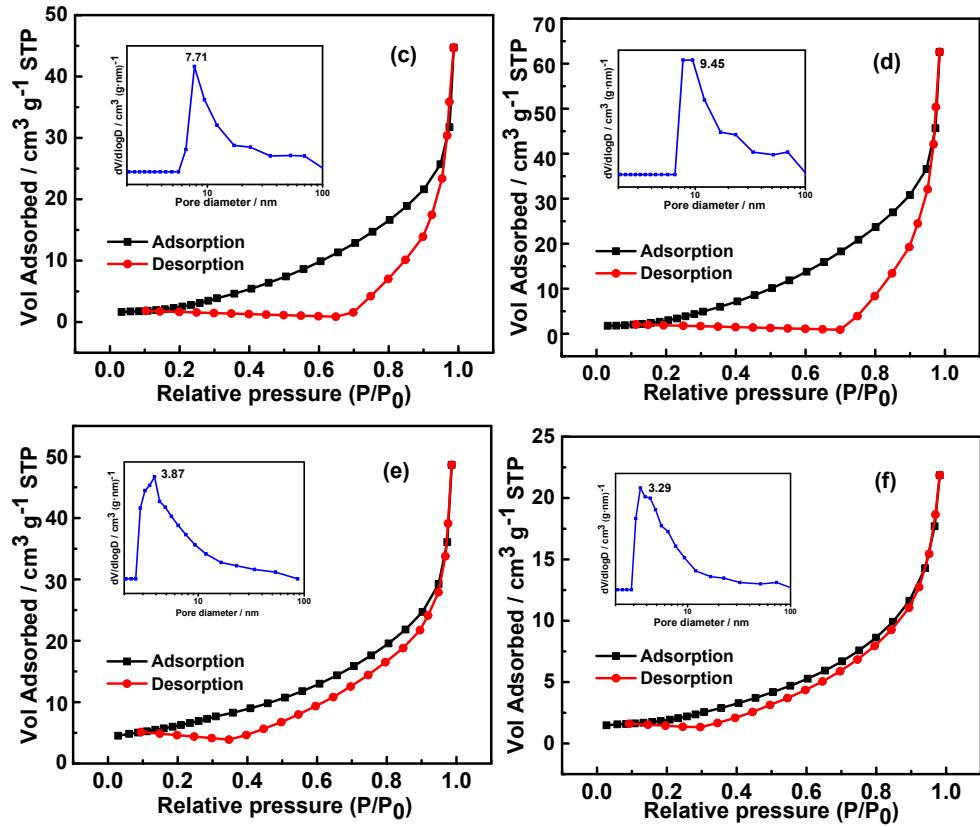
catalyst	Particle size distribution
$\text{Bi}_2\text{O}_3\text{-CuO} (0.5)$	150 nm
$\text{Bi}_2\text{O}_3\text{-CuO} (0.5)$ (reduction))	23 nm
$\text{Bi}_2\text{O}_3\text{-CuO} (0.75)$	28 nm
$\text{Bi}_2\text{O}_3\text{-CuO} (0.75)$ (reduction)	6 nm
$\text{Bi}_2\text{O}_3\text{-CuO} (1.0)$	120 nm



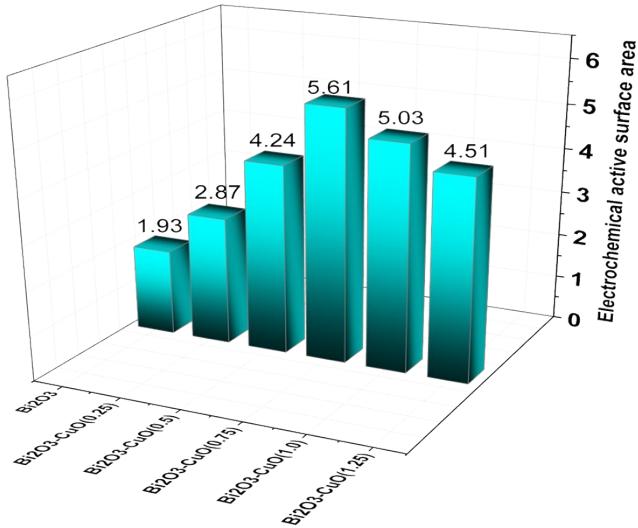
**Fig S 2.** TEM images of  $\text{Bi}_2\text{O}_3\text{-CuO}(x)$ : (A.  $x=0.25$ ; B.  $x=0.75$ ; C.  $x=1.25$ ).

Inset letters a, b, c, d, e represent Lattice interlaced stripes.





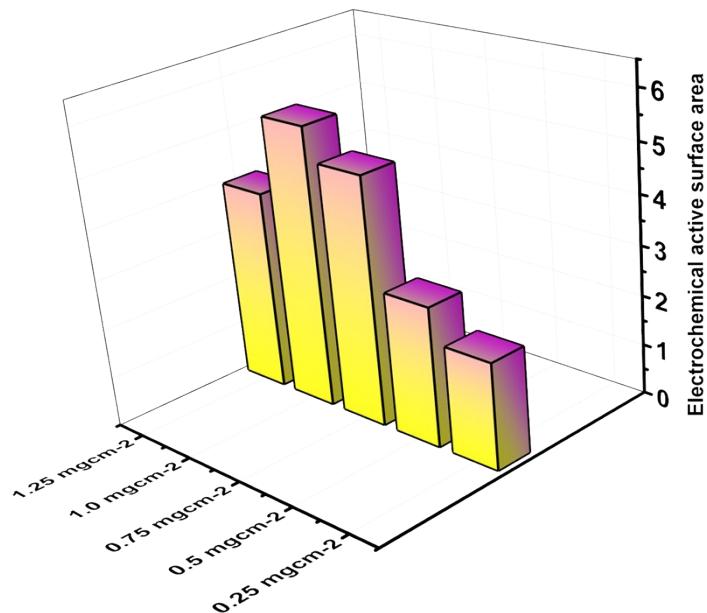
**Fig. S 3.**  $\text{N}_2$  adsorption-desorption isotherms and pore distribution of  $\text{Bi}_2\text{O}_3\text{-CuO}(x)$  catalysts ( $x=0, 0.25, 0.5, 0.75, 1.0, 1.25$ ): (a)=0, (b)=0.25, (c)=0.5, (d)=0.75, (e)=1.0, (f)=1.25



**Fig S 4.** electrochemical active surface area of  $\text{Bi}_2\text{O}_3\text{-CuO}(x)$  catalysts ( $x=0, 0.25, 0.5, 0.75, 1.0, 1.25$ ) with various molar ratio in 0.5 M  $\text{KHCO}_3$  solution

**Table S 2.** The kinetic performance parameters and electrochemical active surface areas of  $\text{Bi}_2\text{O}_3\text{-CuO}(x)$  catalyst ( $x=0, 0.25, 0.5, 0.75, 1.0, 1.25$ ) with various molar ratios for electroreduction of  $\text{CO}_2$

Catalysts	Onset potential (V vs. SCE)	Current density at -1.6 V (mA cm <sup>-2</sup> )	Electrochemical active surface areas (cm <sup>-2</sup> mg <sup>-1</sup> )
Bi <sub>2</sub> O <sub>3</sub>	-1.33	-3.4	1.93
Bi <sub>2</sub> O <sub>3</sub> -CuO(0.25)	-1.31	-6.3	2.87
Bi <sub>2</sub> O <sub>3</sub> -CuO(0.5)	-1.29	-8.6	4.24
Bi <sub>2</sub> O <sub>3</sub> -CuO(0.75)	-1.17	-16.1	5.61
Bi <sub>2</sub> O <sub>3</sub> -CuO(1.0)	-1.26	-14.5	5.03
Bi <sub>2</sub> O <sub>3</sub> -CuO(1.25)	-1.28	-10.1	4.51

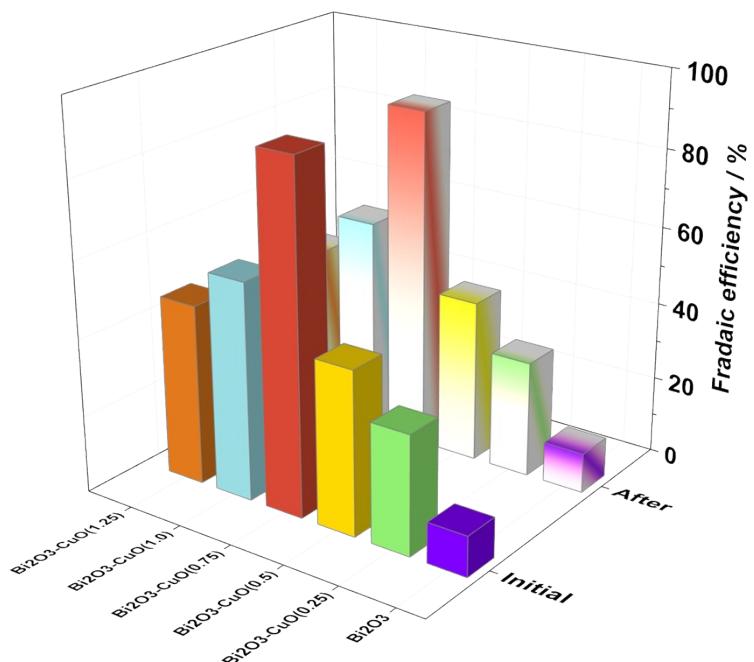


**Fig S 5** electrochemical active surface area of Bi<sub>2</sub>O<sub>3</sub>-CuO(x) catalysts (x=0, 0.25, 0.5, 0.75, 1.0, 1.25) with various loading amounts in 0.5 M KHCO<sub>3</sub> solution

**Table S 3** The kinetic performance parameters and electrochemical active surface areas of Bi<sub>2</sub>O<sub>3</sub>-CuO(0.75) catalyst with various loading amounts for electroreduction of CO<sub>2</sub>

Loading amount (mg.cm <sup>-2</sup> )	Onset potential (V vs. SCE)	Current density at -1.6 V (mA cm <sup>-2</sup> )	Electrochemical active surface areas (cm <sup>-2</sup> mg <sup>-1</sup> )
0.25	-1.38	-4.0	2.12

0.5	-1.31	-8.1	2.79
0.75	-1.29	-13.8	4.96
1.0	-1.17	-16.1	5.61
1.25	-1.31	-12.2	4.02



**Fig. S 6.** FE for formate production before the stability test and after 10 h in  $\text{CO}_2$  saturated 0.5 M  $\text{KHCO}_3$