

## Supporting information

### **Cu-doped $\text{Co}_3\text{O}_4$ nanostructures as an efficient non-noble metal electrocatalyst for methanol oxidation in basic solution**

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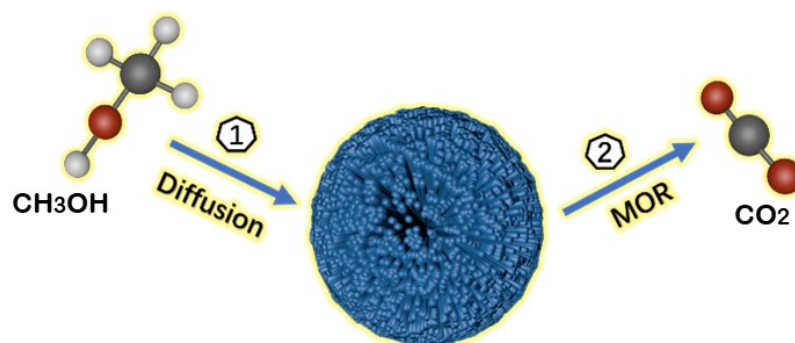
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## Electrochemical tests

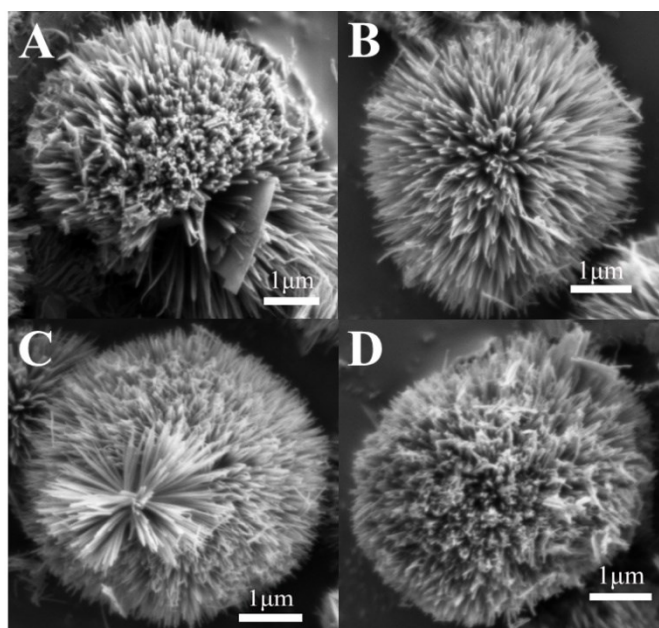
The modified glass carbon electrode (GCE) (3 mm diameter) was used as the working electrode. The counter electrode was a platinum foil (3 cm × 3 cm), and the reference electrode was a saturated calomel electrode (SCE). 4 mg of the obtained electrocatalysts, and 25  $\mu\text{L}$  of Nafion solution (5 wt%) were added into 475  $\mu\text{L}$  of methanol solution to form a homogeneous suspension by ultrasonication. Then, the ink (5  $\mu\text{L}$ ) was dropped on the surface of the working electrode and dried naturally at ambient temperature. The loading capacity of the catalysts ( $0.142 \text{ mg cm}^{-2}$ ) was kept constant for all the samples to comparatively investigate. The current density of MOR were calculated according to the geometric area of the GCE.

Cyclic voltammograms (CVs) were performed in  $\text{N}_2$ -saturated KOH solution at 50 mV/s scan rate, and the electrochemical active surface areas (ECSAs) of catalyst samples were determined from the double-layer capacitance in the CVs. The CVs for MOR were conducted in  $\text{N}_2$ -saturated solution containing 1 M KOH and 1 M  $\text{CH}_3\text{OH}$  between 0 and 1.0 V vs. SCE at 50 mV/s scan rate. As for MOR stability, it tests were performed at the 0.6 V fixed potential vs. SCE. Impedance spectroscopy (EIS) was carried out using GCE (frequency 100 kHz to 1 Hz).

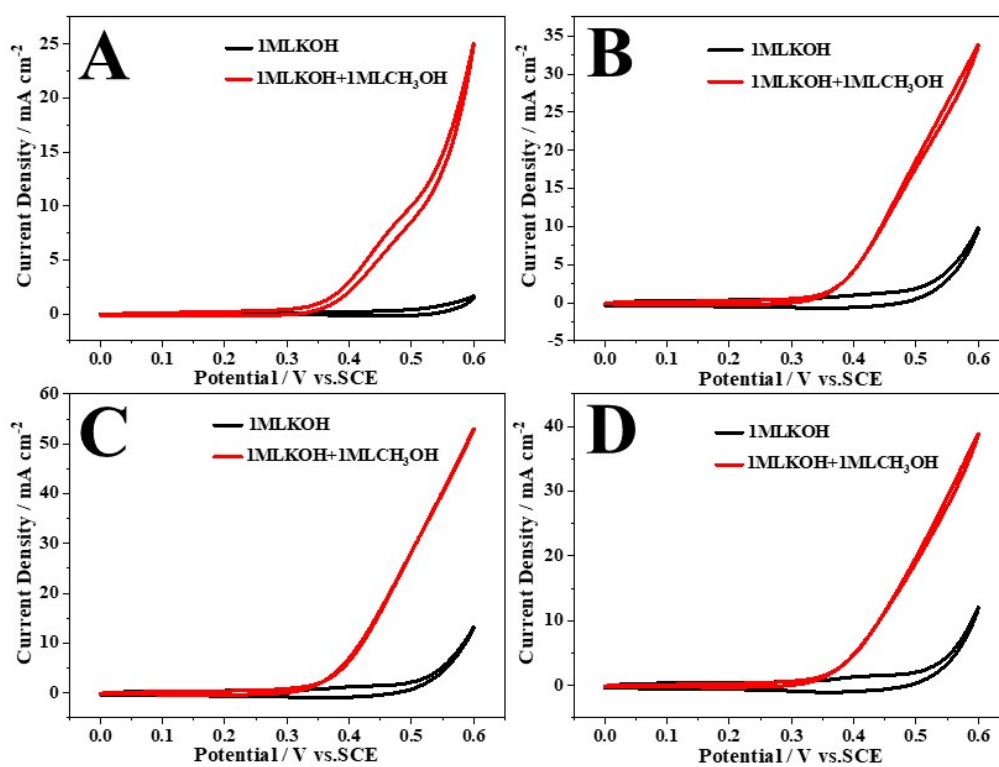


Nanoflowers doped with copper cobalt tetroxide catalyst were synthesized by a simple method for electrocatalytic oxidation of methanol applications. By virtue of compositional and structural control, the electrocatalytic activity of the 15 % CuCo<sub>3</sub>O<sub>4</sub> nanocomposites can be significantly improved for methanol oxidation. Moreover, 15 % Cu-Co<sub>3</sub>O<sub>4</sub> nanocomposites demonstrated the strong ability to resist CO poisoning under alkaline conditions, suggesting the excellent stability.

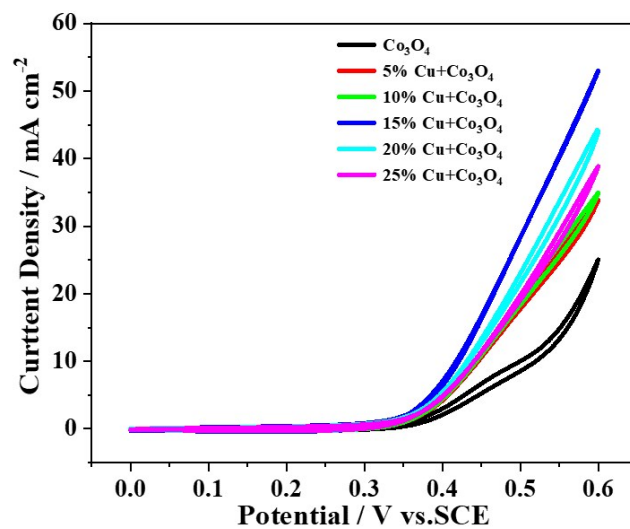
The methanol reaction on the electrode surface is a two-way reaction, Methanol was first dissociated and adsorbed on the electrode surface to form toxic intermediate CO, and then regenerated to CO<sub>2</sub>. Copper doping, on the one hand, can affect the electronic state of Co, thus weakening the interaction between Co and CO. what's more, copper doping can produce more active sites, promoting the oxidation of intermediate species adsorbed by methanol disintegration, and thus improving the electrocatalytic performance and anti-poisoning performance of Co<sub>3</sub>O<sub>4</sub> for methanol oxidation.



**Fig. S1.** SEM images of  $\text{Co}_3\text{O}_4$  (A), 5%  $\text{Cu-Co}_3\text{O}_4$  (B), 15%  $\text{Cu-Co}_3\text{O}_4$  (C), 25%  $\text{Cu-Co}_3\text{O}_4$  (D).



**Fig. S2.** CV curves of  $\text{Co}_3\text{O}_4$  (B) 5%  $\text{Cu-Co}_3\text{O}_4$  (C) 15%  $\text{Cu-Co}_3\text{O}_4$  (D) 25%  $\text{Cu-Co}_3\text{O}_4$  (E) respectively towards MOR in 1 M KOH and 1 M  $\text{CH}_3\text{OH}$ .



**Fig. S3.** CV curves of Co<sub>3</sub>O<sub>4</sub>, 5% Cu-Co<sub>3</sub>O<sub>4</sub>, 10% Cu-Co<sub>3</sub>O<sub>4</sub>, 15% Cu-Co<sub>3</sub>O<sub>4</sub>, 20% Cu-Co<sub>3</sub>O<sub>4</sub>, 25% Cu-Co<sub>3</sub>O<sub>4</sub> towards MOR in 1 M KOH + 1 M CH<sub>3</sub>OH (B).