

## Supporting Information

### Experiments

The preparation procedure of  $\text{Cu}_1\text{Au}_{0.15}\text{Pd}_{1.5}/\text{C}$  catalyst is under a moderate wet chemistry method. First, 39.3 mg (0.15 mmol)  $\text{Cu}(\text{acac})_2$ , 68.5 mg (0.225 mmol)  $\text{Pd}(\text{acac})_2$  and 30 mg  $\text{PVP}_{\text{K}30}$  were dissolved in 40 mL ethylene glycol (EG) in the nitrogen atmosphere, then the mixture was heated to 80 °C under stirring for 1.5 hours. Add 9.2 mg  $\text{AuCl}_3 \cdot 4\text{H}_2\text{O}$  and maintained for 0.5 hour. The obtained  $\text{Cu}_1\text{Au}_{0.15}\text{Pd}_{1.5}$  solution was washed by ethanol and acetone for 3 times and dispersed in ethanol. 70 mg Vulcan XC-72 was added followed by vigorous stirring under 75 °C to remove the ethanol. The resulting catalyst was subjected to  $\text{N}_2$  at 200 °C for 3 hours to get the  $\text{Cu}_1\text{Au}_{0.15}\text{Pd}_{1.5}/\text{C}$  catalyst. The Pd/C catalyst was prepared in the same way using only  $\text{Pd}(\text{acac})_2$  as metal source.

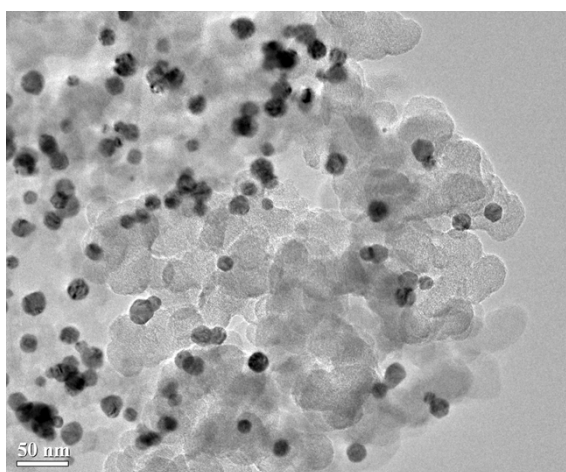


Fig. S1. TEM image for Pd/C

### Electrochemical measurements

All the electrochemical measurements were conducted on the CHI 660A electrochemical workstation (Shanghai Chenhua apparatus corporation, China) using a conventional three-electrode glassy cell with a platinum sheet and an  $\text{Hg}/\text{HgO}/\text{OH}(\text{KOH } a=1)$  electrode (mercuric oxide electrode, 0.098 V vs. NHE) as the counter and reference electrodes.

To confirm the long-term durability of Pd/C and  $\text{Cu}_1\text{Au}_{0.15}\text{Pd}_{1.5}/\text{C}$  catalysts toward ethanol oxidation, chronoamperometry experiments were performed for a duration of 1000 s. Fig. S2 shows the current - time curves for the two catalysts, both electrodes display a current decay during the initial period because of the formation of intermediate species such as  $\text{CH}_3\text{OH}_{\text{ads}}$  and  $\text{CHO}_{\text{ads}}$ . On the Pd/C electrode, there's a fast decay in the initial 300s and reaches 18  $\text{mA mg}^{-1}\text{Pd}$  at 1000s. The rate of current decay is much slower for  $\text{Cu}_1\text{Au}_{0.15}\text{Pd}_{1.5}/\text{C}$  and it maintains 250  $\text{mA mg}^{-1}\text{Pd}$  at 1000s, indicating that  $\text{Cu}_1\text{Au}_{0.15}\text{Pd}_{1.5}/\text{C}$  has the superior catalytic stability for ethanol oxidation. This result is in agreement with the behaviors in other electrochemical experiments.

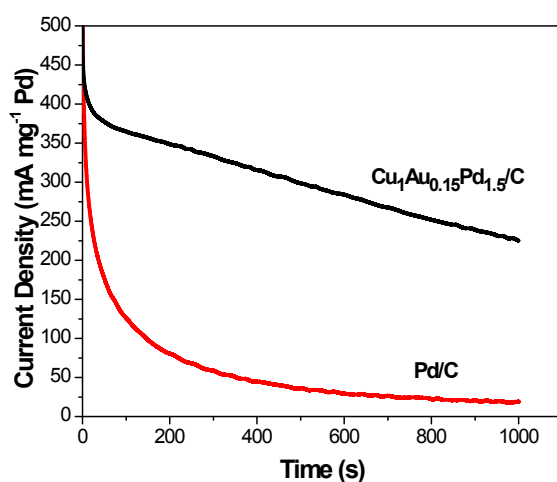


Fig. S2. Chronoamperometry curves polarizing at  $-0.1$  V.

### Electrochemical discussion

We have also fabricated the CuPd/C catalyst and found it even worse than the Pd/C catalyst. Through some electrochemical measurements we found it's mostly probable that the Cu will form Cu-O(H) species to shelter the active sites on the surface of CuPd particles in alkaline media. Fig. S3A shows the CV cycles in 0.5 M KOH and Fig. S3B shows the subsequent CV cycles in 0.5 M KOH and ethanol on CuPd/C electrode. We can hardly see the oxidation peak of ethanol. The cathodic peak around  $-0.2$  V will keep enlarging along with the cycles increasing, which may due to the in-situ formed Cu-O(H) species.

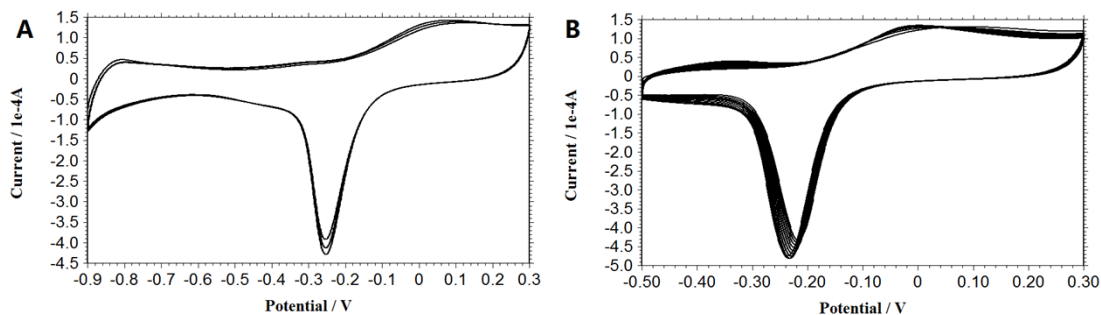


Fig. S3 (A) CV cycles in 0.5 M KOH on CuPd/C electrode. (B) CV cycles in 0.5 M KOH and 0.5 M ethanol following the tests in Fig S3A on CuPd/C electrode

Moreover, we conducted the experiment in the 0.5 M  $H_2SO_4$  followed by ethanol oxidation in alkaline media. From Fig. S4A we can clearly see the oxidation peak of Cu in the red block. After the cycles in acid solution, we conducted the ethanol oxidation in alkaline electrolyte and found the PdCu/C did show catalytic activity after the dealloying in the sulfuric acid. Even so, the catalyst shows a rapid decay in only 10 cycles. What's more, we found the more sufficient dealloying, the higher peak current we will get. The above electrochemical results seem to confirm the speculation that the Cu on the surface of PdCu will form Cu-O(H) species and hinder the catalysis of ethanol oxidation in alkaline media. We found the literature proof from a new publication (Zhang, Q.-L., Zheng, J.-

N., Xu, T.-Q., Wang, A.-J., Wei, J., Chen, J.-R., & Feng, J.-J. *Electrochimica Acta*, 132(0), 551-560. ). In this article, the Pd-on-Cu/RGO shows higher catalytic activity than simple PdCu/RGO, which is in agreement with our conjecture that the surface Cu will hinder the Pd active sites. So we came to a conclusion that unless the surface Cu is removed in acidic solution beforehand, otherwise the Pd active sites may soon be covered, leading to a fast fading of the catalyst.

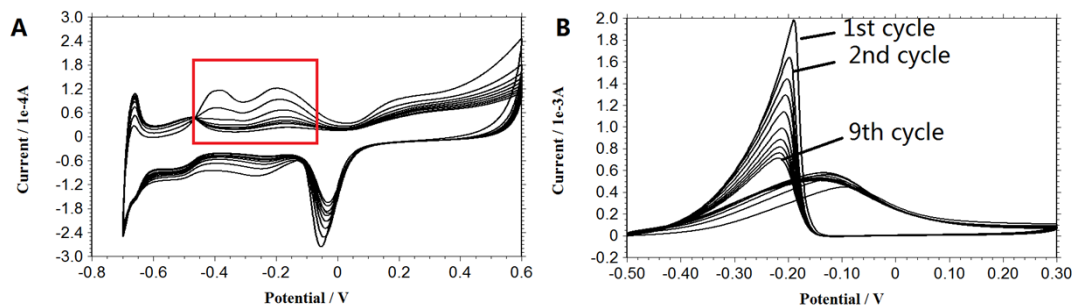


Fig. S4 (A) CV cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub> on CuPd/C electrode. (B) CV cycles in 0.5 M KOH and 0.5 M ethanol just after the tests in Fig S4A on CuPd/C electrode

Besides, we find our Cu<sub>1</sub>Au<sub>0.15</sub>Pd<sub>1.5</sub>/C does not show the Cu oxidation peak in sulfuric acid (Fig. S5). We deem that there's hardly any exposed Cu on the surface of Cu<sub>1</sub>Au<sub>0.15</sub>Pd<sub>1.5</sub>, we fabricated the CuPd NPs and then used the HAuCl<sub>4</sub> to replace the Cu on the surface, and this also agrees with the XPS results that Pd and Au are more enriched on the surface compared to the bulk composition. One of the important roles for Au is to replace the outer Cu and hinder the Cu from forming the Cu-O(H) species.

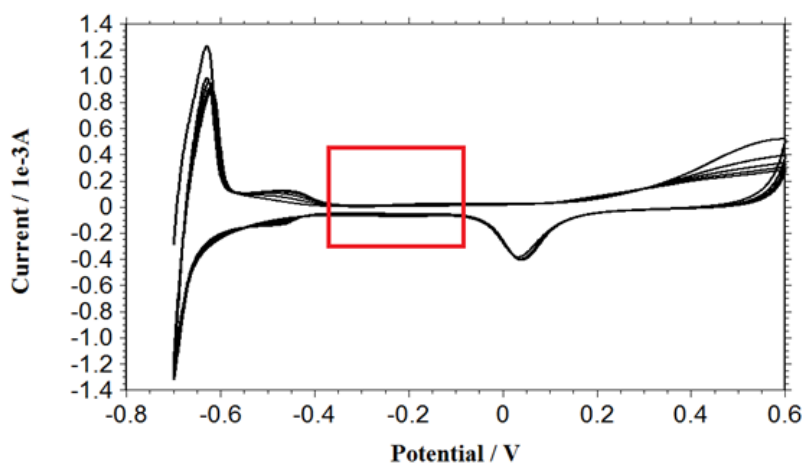


Fig. S5 First ten CV cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub> on Cu<sub>1</sub>Au<sub>0.15</sub>Pd<sub>1.5</sub>/C electrode.