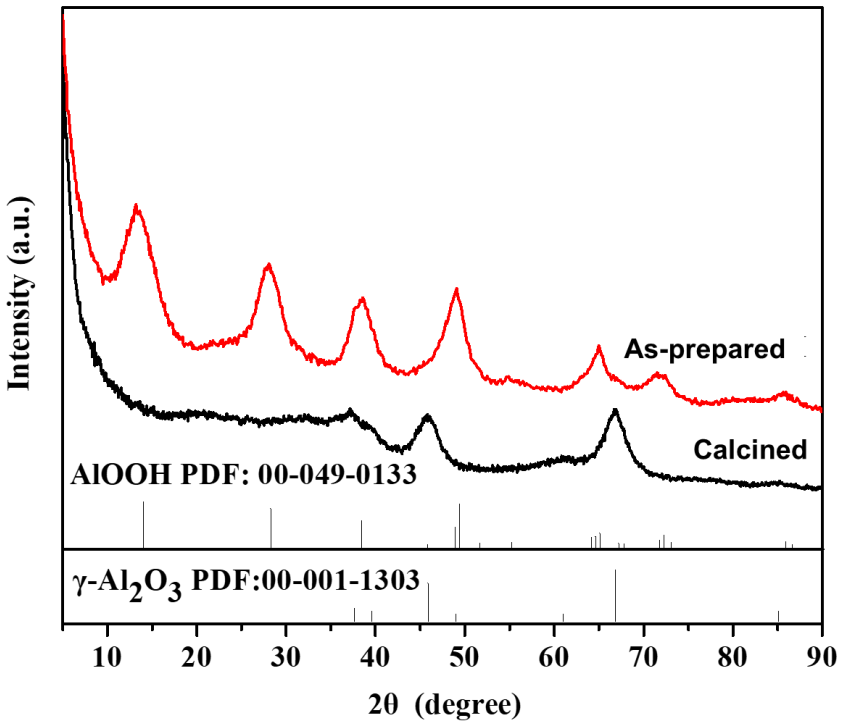
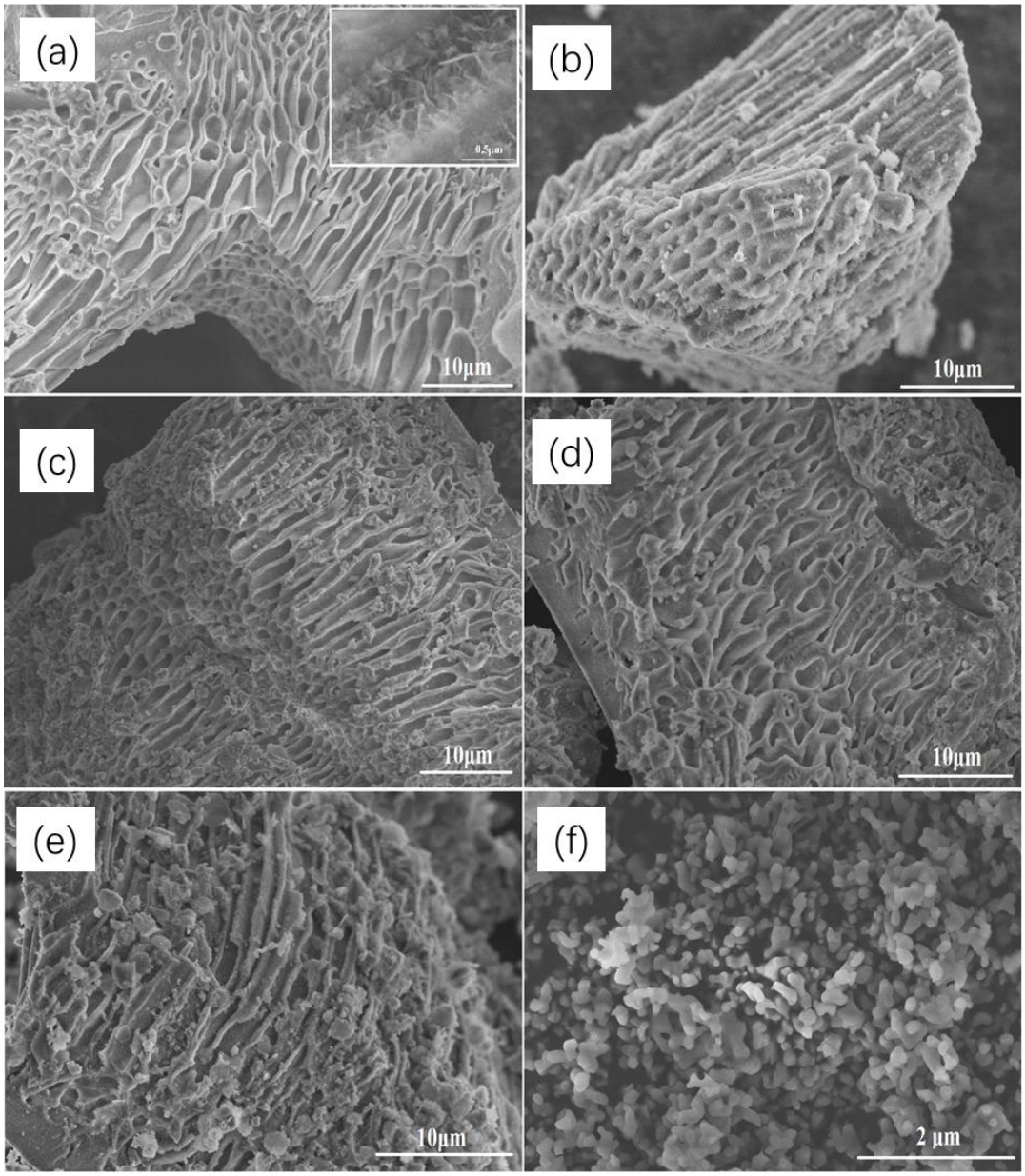
Supplementary Material:

Figure S1 XRD of as-prepared and calcined hierarchically porous alumina.



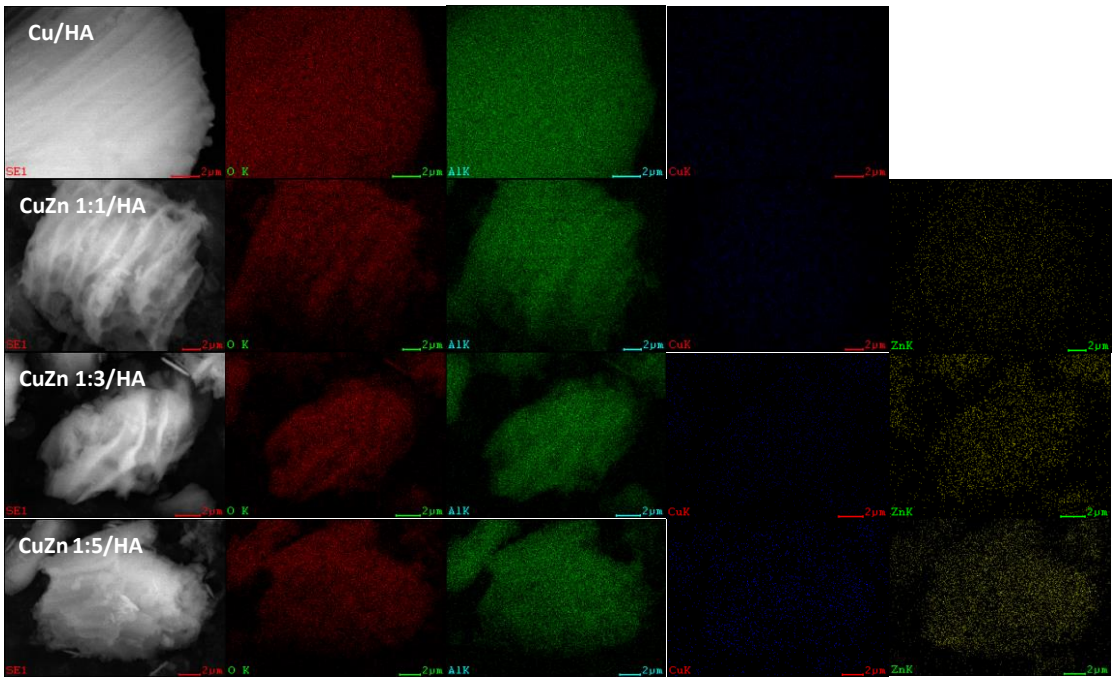
It can be found that AlOOH was formed after the hydrolysis and condensation of aluminum sec-butoxide. And it transformed to γ-Al_2O_3 after calcination at 500^{o}C for 2h.

Figure S2 SEM of HA (a), Cu/HA(b), Cu1Zn1/HA(c), Cu1Zn3/HA(d), Cu1Zn5/HA(e) and Cu/commercial bulky alumina(f).



It can be found that the deposition-precipitation of Cu^{2+} and Zn^{2+} have limited effect on the hierarchically porous structure of alumina support. Some fragments were observed in the Cu-Zn/HA samples, especially in Cu1Zn5/HA sample. This might be the main reason for the decrease of total surface area of samples, as it was presented in Table 1.

Figure S3 SEM-EDS of Cu/HA, Cu1Zn1/HA, Cu1Zn3/HA and Cu1Zn5/HA.



SEM-EDS shows that Cu and Zn highly disperses on the surface of hierarchically porous alumina. Moreover, the fragments observed by SEM is mainly alumina, instead of copper-zinc compounds.

Figure S4 Particle size distribution. (a) Cu/CA; (b) Cu/HA; (c) Cu1Zn1/HA; (d)Cu1Zn3/HA; (e) Cu1Zn5/HA after calcination at 400ºC for 2h then reduction at 350ºC for 2h.

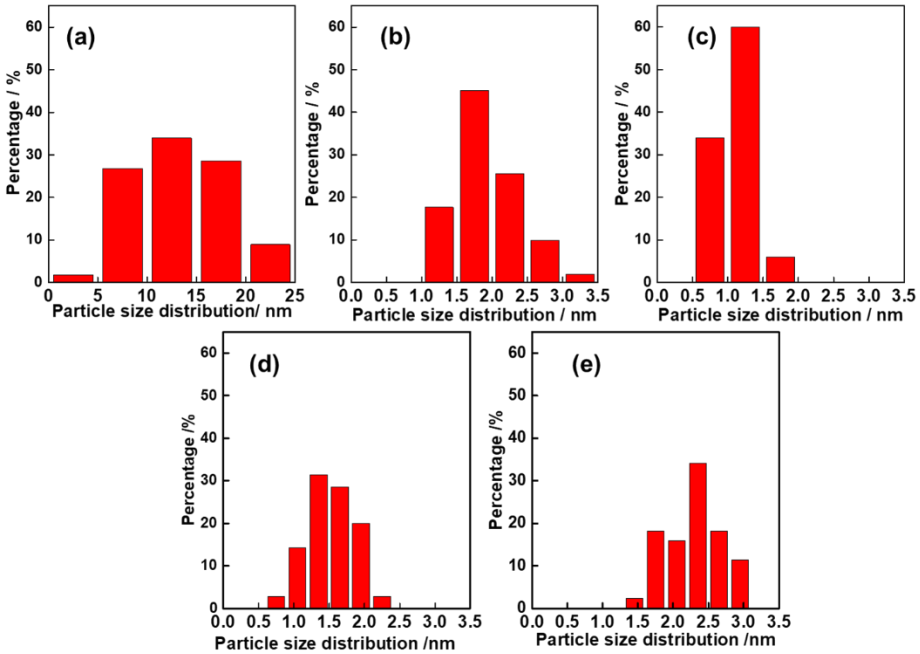
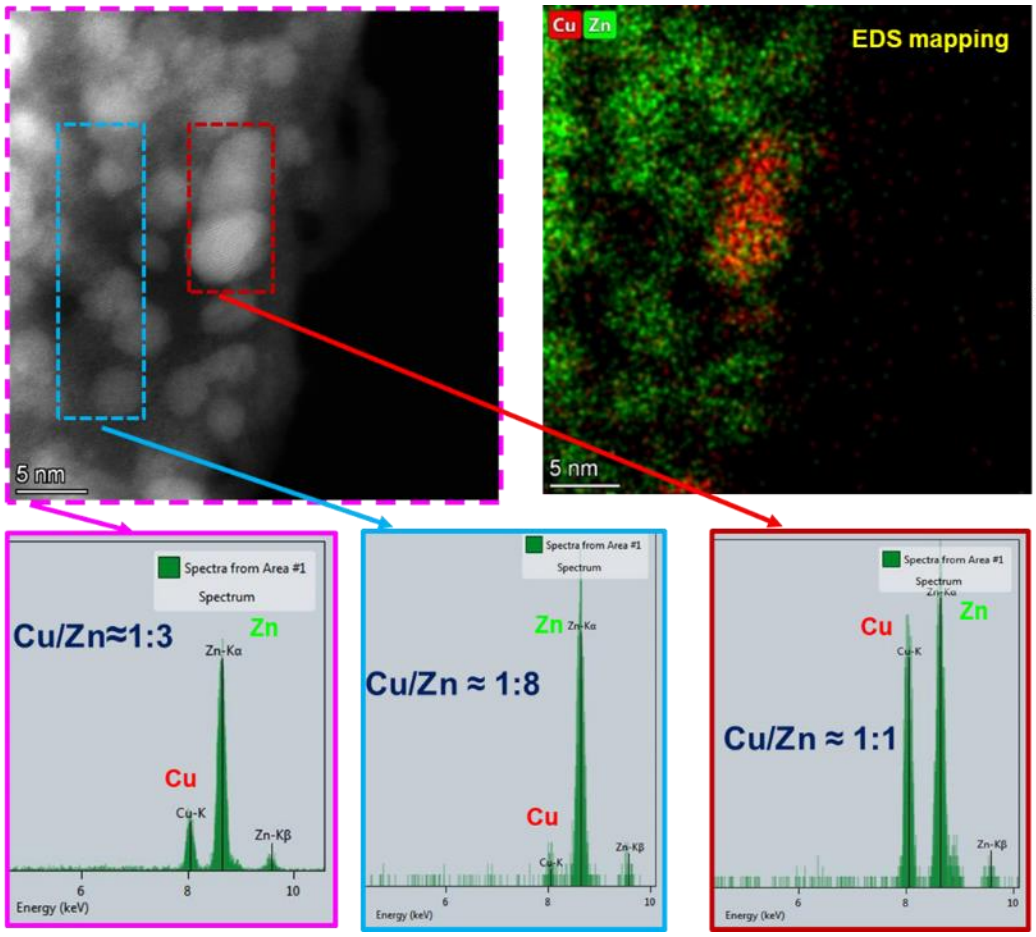


Figure S5 STEM-HAADF coupled with EDS on the reduced Cu1Zn3/HA.



EDS of the whole area shows the Cu/Zn atomic ratio is around 1:3, which agrees with the nominal Cu/Zn ratio in Cu1Zn3/HA sample. Moreover, EDS mapping shows two different areas, i.e., Cu-rich area and Zn-rich area, exist in the sample. Specifically, in the Cu-rich area, large particle was identified, with diameter around 4-5nm. The Cu/Zn atomic ratio is close to 1:1, which agrees with the results of XRD and the EDS dotting in Figure 4f. However, as for the Zn-rich area, Cu/Zn atomic ratio is 1:8. The un-identified Zn/ZnO particle in the sample by XRD indicates that the state of Zn might be amorphous, or a thin film on alumina.

Figure S6 TG analysis of Cu/CA and Cu-Zn/HA samples after stability test.

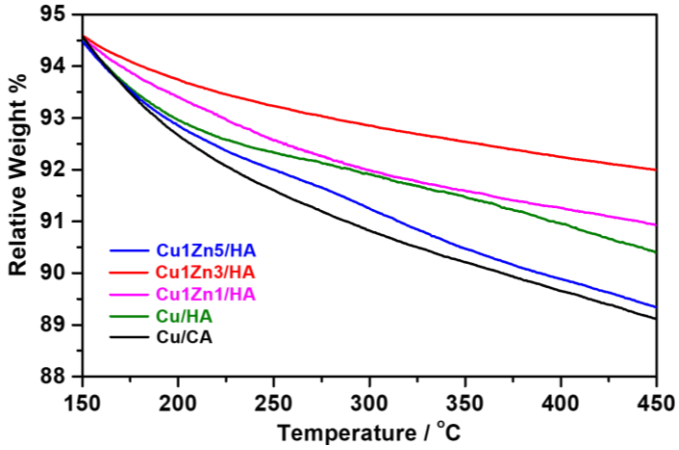
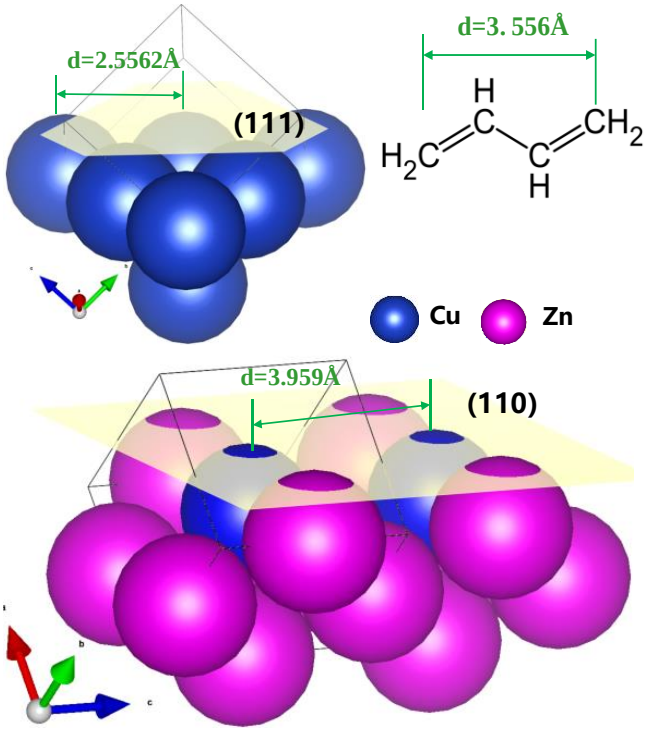


Figure S7 the (111) and (110) crystal surface of metallic Cu (JCPDS:85-1326) and Cu-Zn alloy (JCPDS:65-9061).



The crystal structure of metallic Cu and Cu1Zn1 alloy was simulated by the VESTA software based on the JCPDS card from XRD. It can be found that the distance between two neighbored copper atoms is 2.5562 Å and 3.959Å for the (111) of metallic Cu and the (110) of Cu1Zn1 alloy, respectively. Moreover, the length of butadiene molecular is 3.556 Å. Therefore, the butadiene molecular can adsorbed on two neighbored copper atoms in monometallic Cu, but can not adsorbed on two neighbored copper atoms in Cu-Zn alloy.