Supporting information

Construction of CuCo bimetallic nanoparticles on perovskite oxide $LaFeO_3$ for efficient hydrogen production from ammonia borane hydrolysis

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1. Experimental section

1.1. Materials

All chemicals were purchased from commercial sources and used without further purification. Copper(II) nitrate hexahydrate ($Cu(NO_3)_2 \cdot 6H_2O$,SCR.Co.,), Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 3H_2O$,SCR.Co.,)sodium borohydride ($NaBH_4$,SCR.Co.,96%), Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$,SCR.Co.), Iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$,Macklin.Co.,98.5%), Lanthanum nitrate hexahydrate($La(NO_3)_3 \cdot 6H_2O$, Macklin.Co.,99%), Ammonia borane(NH_3BH_3, Macklin.Co.,).

1.2. Preparation of $LaFeO_3$

$LaFeO_3$ nanoparticles were synthesized using the citric acid Piccini sol-gel method. A stoichiometric mixture of $La(NO_3)_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ with the concentration of 0.2 M, was added to a solution containing 50 mL of deionized water along with 0.4 M $C_6H_8O_7 \cdot H_2O$, and stirred for one hour until the solution became clear, transparent, and stable. Subsequently, 7-8 mL of ammonia hydroxide ($NH_3 \cdot H_2O$) solution was introduced to adjust the pH to between 6 and 7. After an additional hour of stirring, the temperature in the water bath was maintained at 80°C while stirring continued for another 3-4 hours until a sol formed. The resulting gel was dried in an oven at 60°C for approximately 18 hours before being ground for 30 minutes. The finely powdered dry gel was then uniformly placed in a muffle furnace; it was first heated from room temperature to 200°C at a rate of 5°C/min over a period of twelve hours, followed by heating from 200°C to 600°C at the same rate over five hours before allowing it to cool naturally to yield $LaFeO_3$ powder. Finally, the sample powder was preserved in a vacuum drying oven.

1.3. Procedure for the hydrolytic dehydrogenation of AB

In general, the synthesized catalyst-aqueous solution mixture is introduced into a two-necked round-bottom flask (50 ml), which is then placed in a water bath maintained at a predetermined temperature ranging from 25°C to 50°C. The AB aqueous solution is subsequently injected into the mixture using a syringe to initiate the reaction under controlled conditions. A gas collection tube filled with water is connected to the reaction flask, and the temperature is consistently maintained at 50°C to facilitate measurement of the volume of gas released during the reaction. The volume of gas produced is monitored by recording the displacement of water within the gas collection tube as the mixture undergoes injection via syringe. The completion of the reaction is indicated when there are no further increases in gas volume observed. In all catalytic reactions, it should be noted that the molar ratio of (Cu+Co)/AB remains theoretically fixed at 0.05.

The turnover frequency (TOF) in this work is an apparent TOF value based on the number of CuCo atoms in catalyst, which is calculated from the equation as follow:

$\mathrm{TOF} = P_0V/(RTn_{\mathrm{CuCo}}t)$

Where P_0 is the atmospheric pressure (101325 Pa), V is the volume of generated hydrogen, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the reaction temperature (K), n_{CuCo} is the total mole number of CuCo atoms in catalyst, and t is the reaction time.

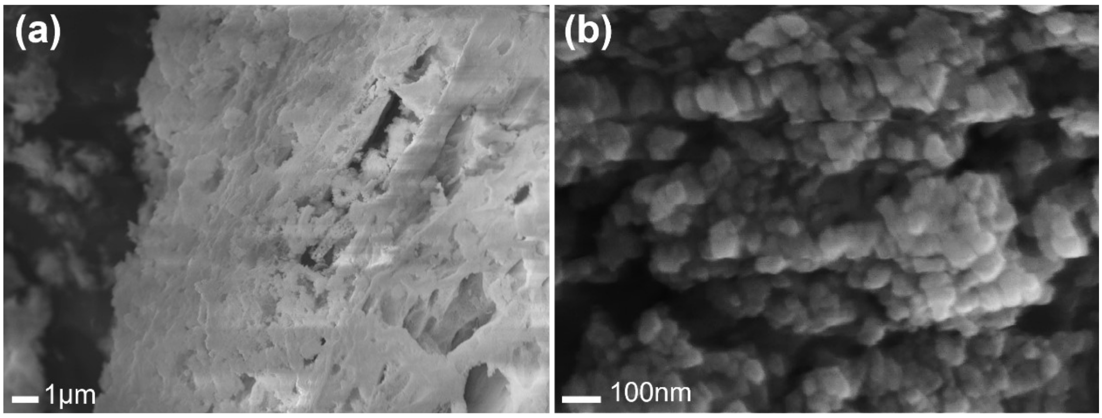

Figure S1. SEM morphology images of CuCo/$LaFeO_3$.

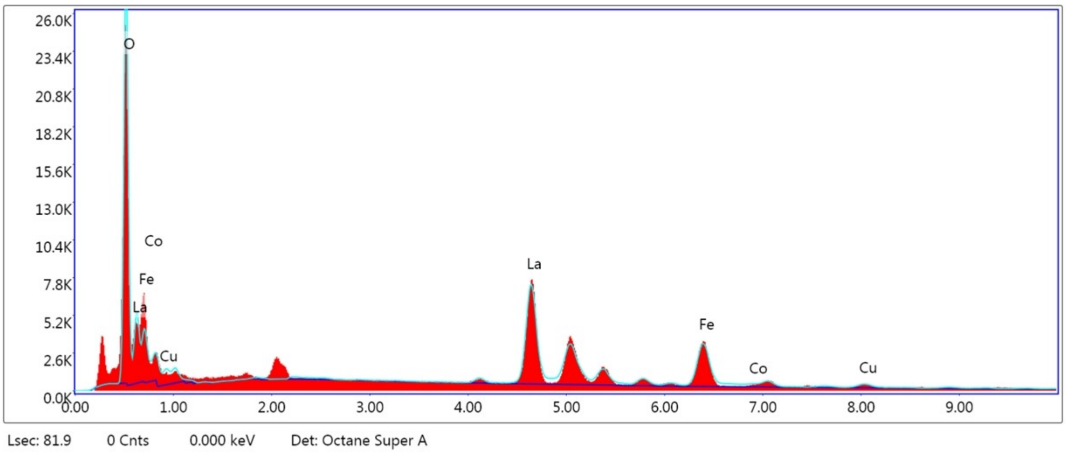

Figure S2. EDTX spectrum of $CuCo/LaFeO_3$

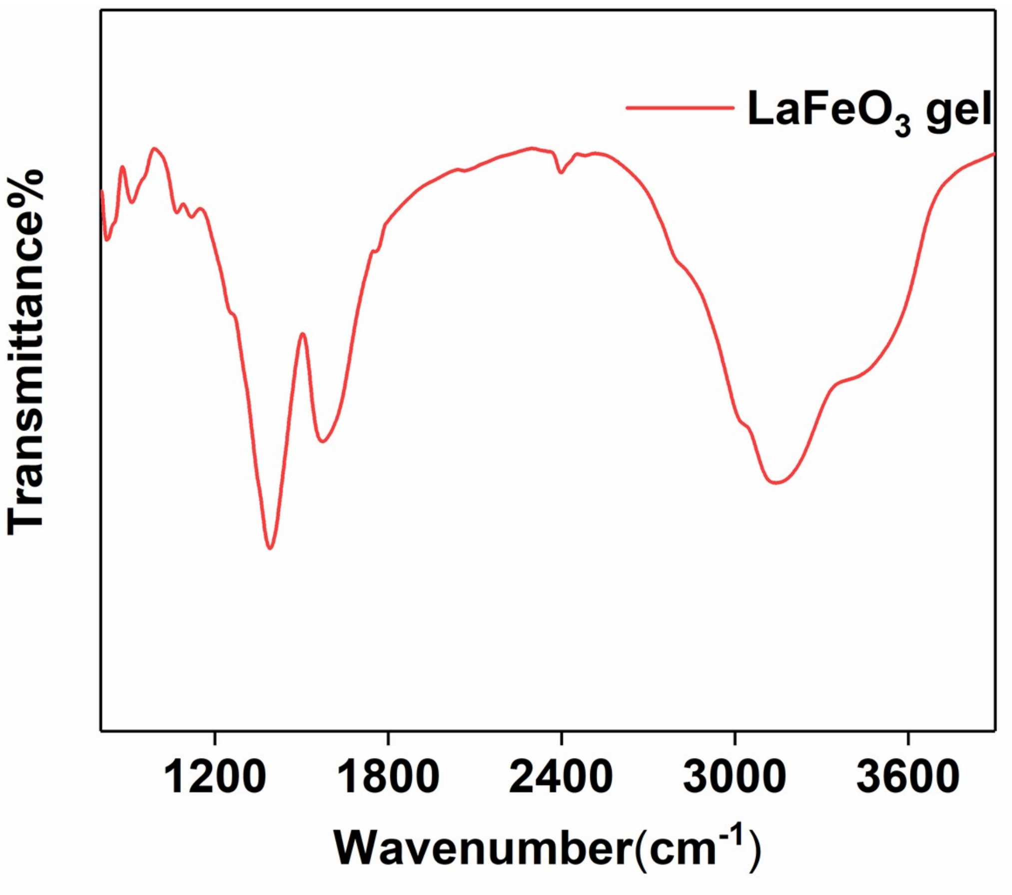

Figure S3. Infrared spectrum of LaFeO$_3$ gel.

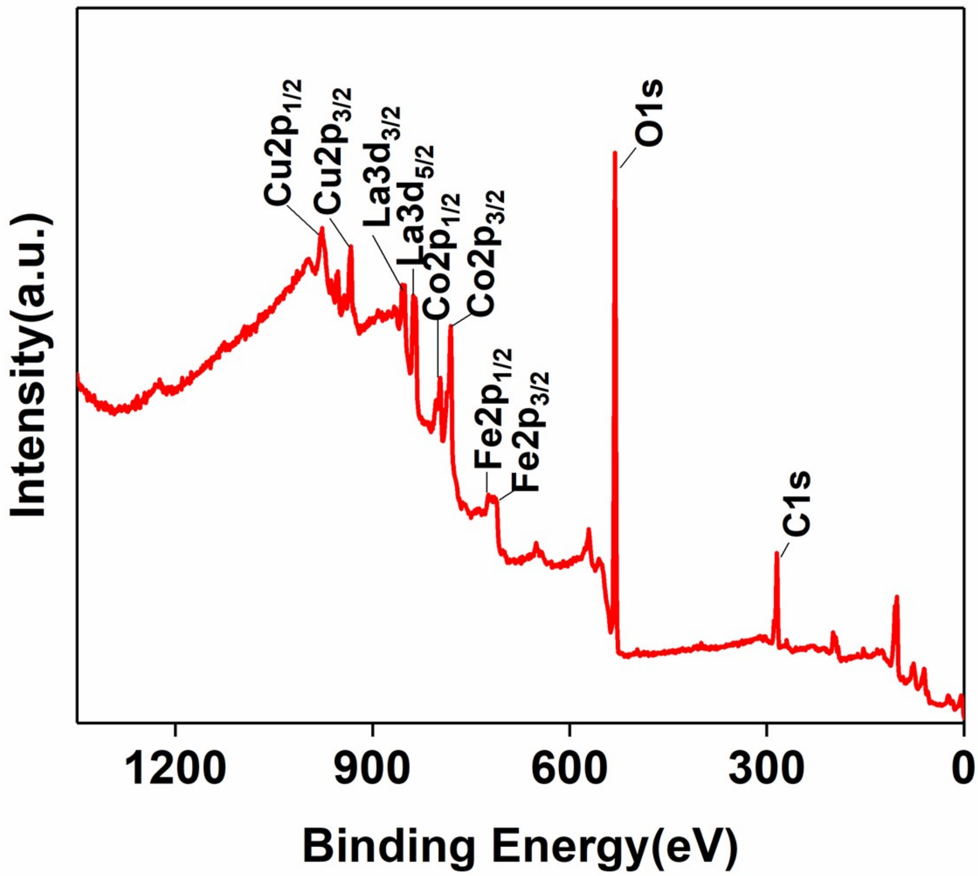

Figure S4. XPS full spectrum of CuCo/$LaFeO_3$.

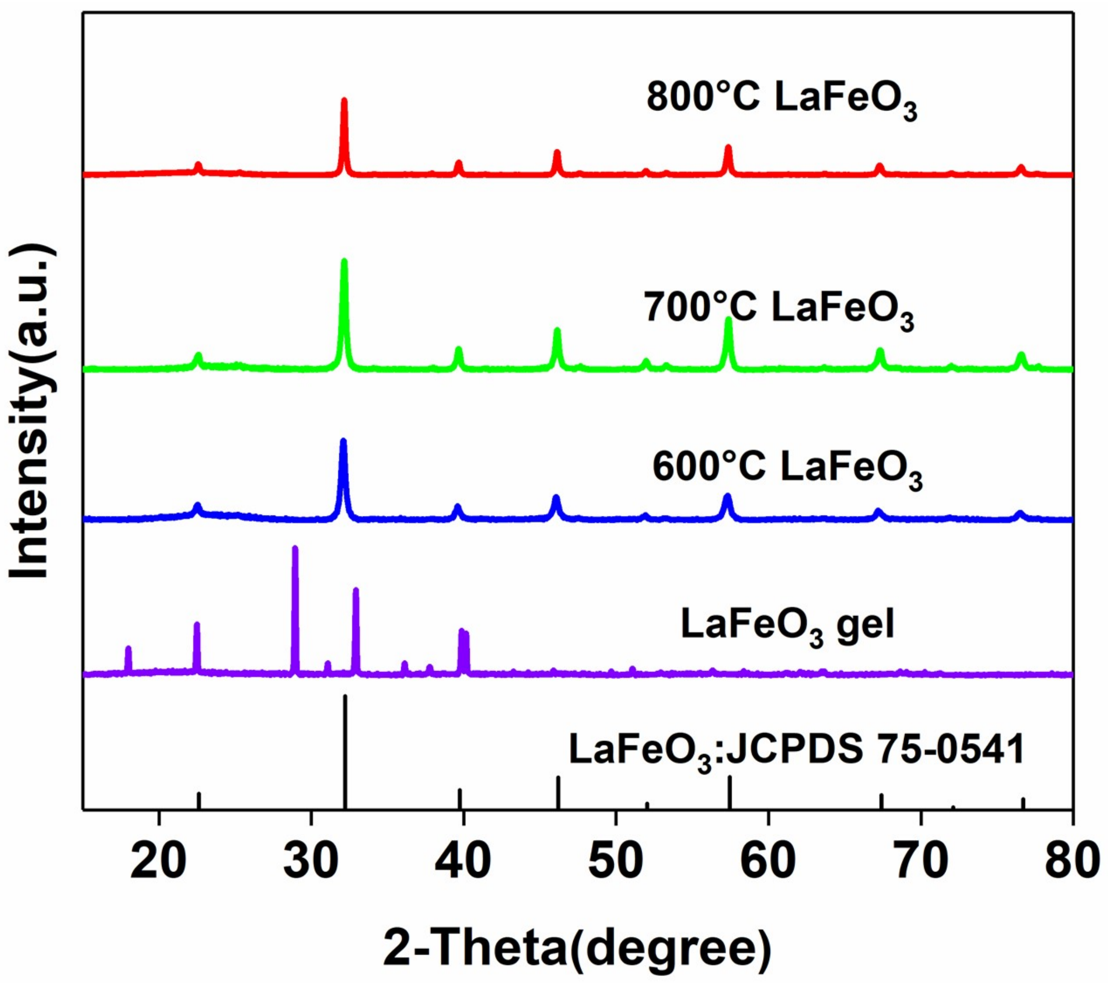

Figure S5. XRD patterns of gel precursor and LaFeO$_3$ calcined at different temperatures

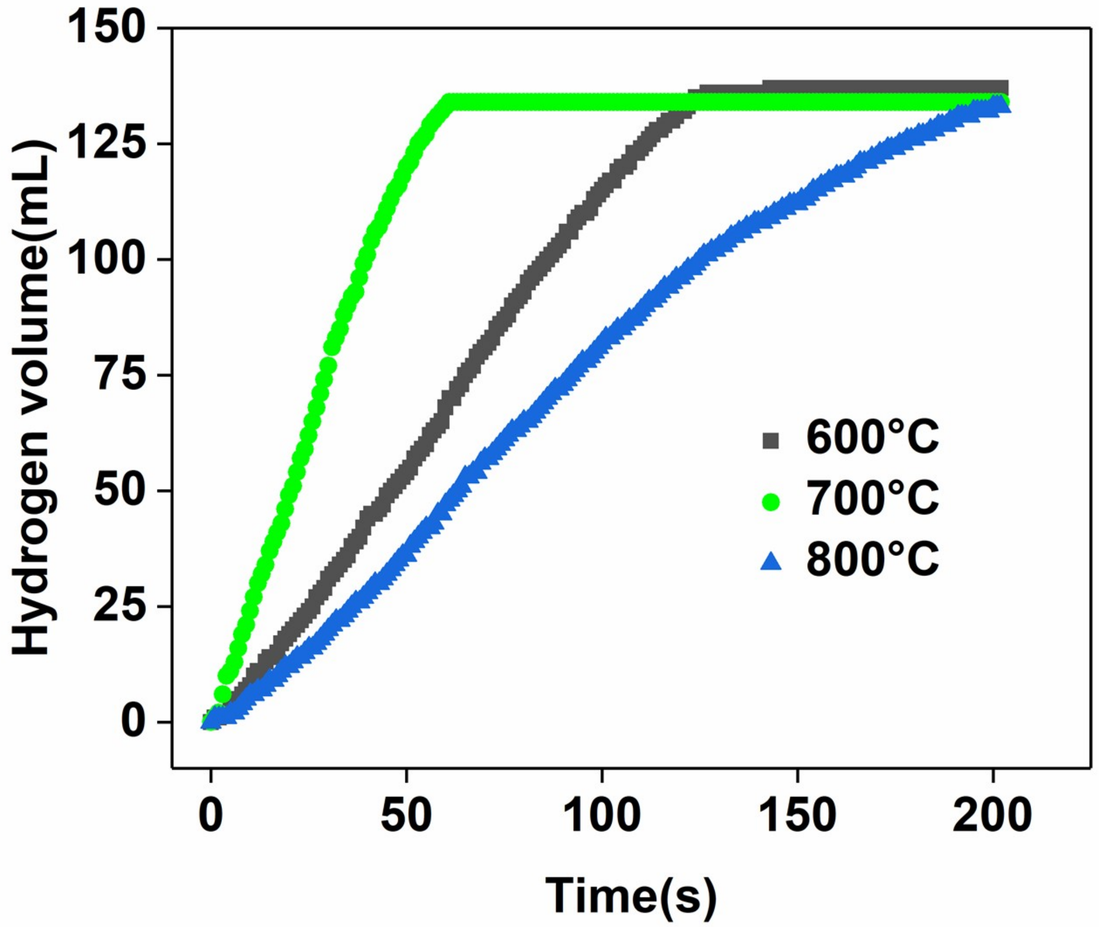

Figure S6. Catalytic AB hydrolytic hydrogen production of $LaFeO_3$@CuCoNPs prepared at different sintering temperatures.

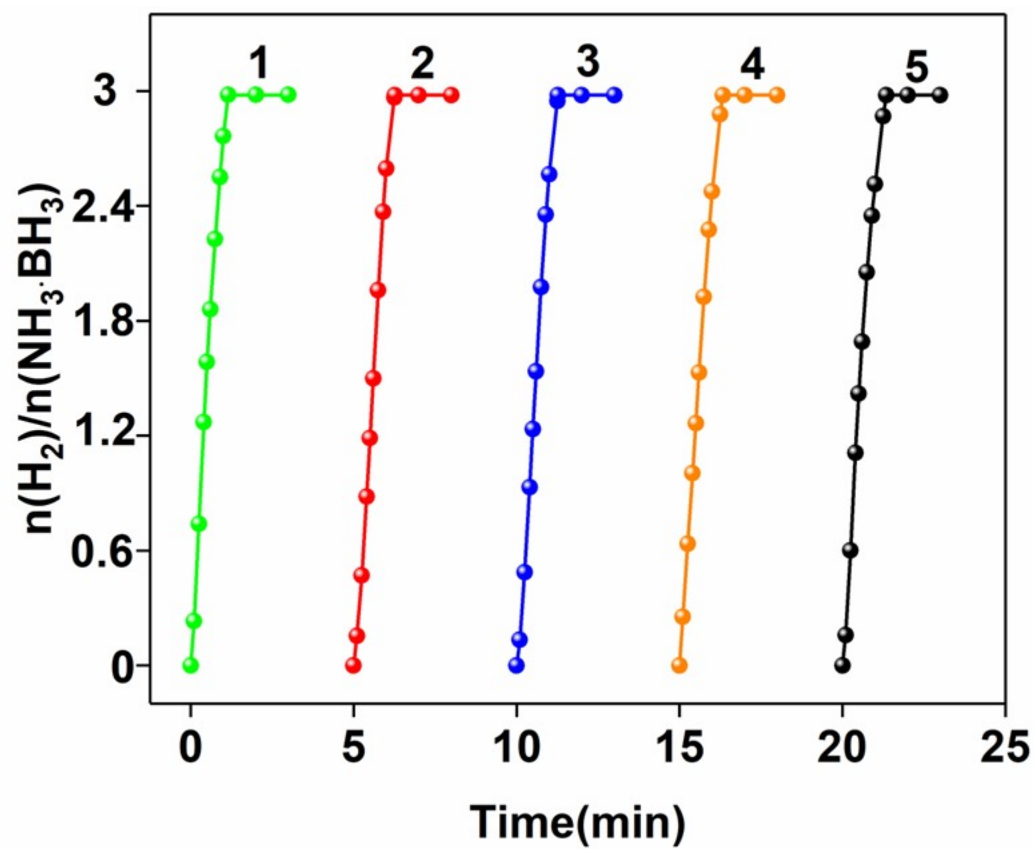

Figure S7 Comparison of ABH over $Cu_{0.4}Co_{0.6}/LaFeO_3$ for five consecutive catalytic cycle.