

## Supporting Information

### **La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>-induced phase composition oscillation for La-Cu mixed oxides during repeated catalytic soot combustion**

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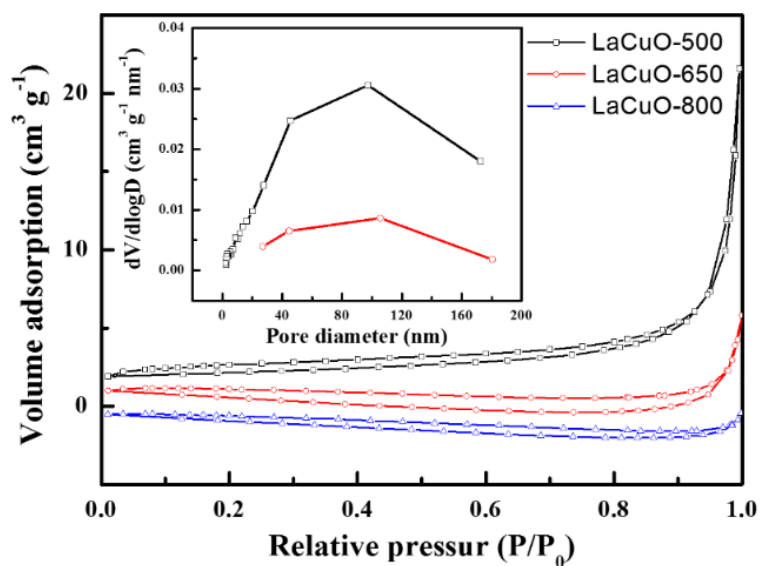
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## Figures & Tables

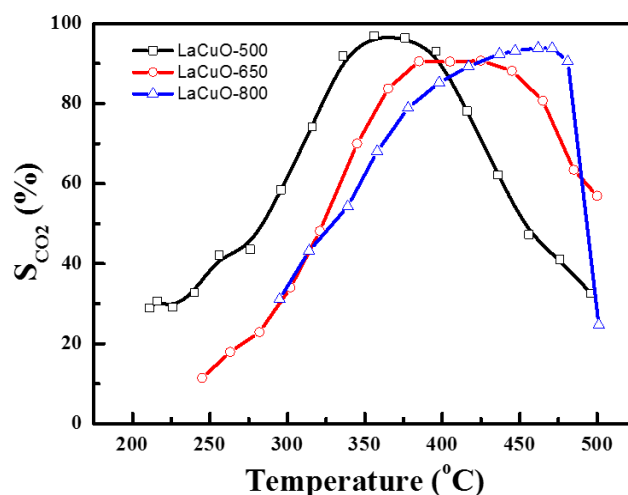


**Fig. S1.** N<sub>2</sub> adsorption-desorption curves and (inset) pore size distribution curves of LaCuO-*x*. (*x* = 500, 650, 800) Note that the pore size distribution curve of LaCuO-800 is absent due to its scarce pore structures.

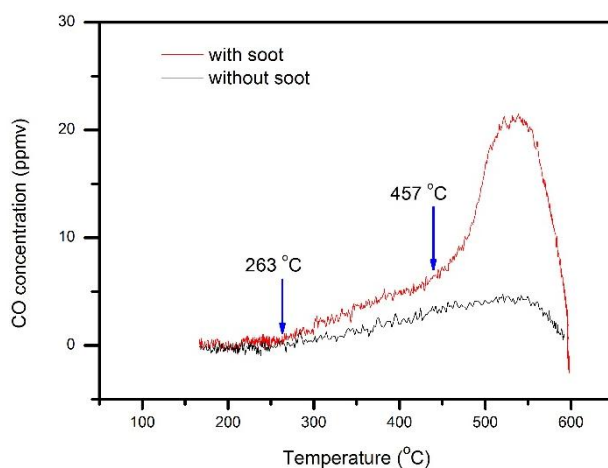
**Table S1.** The characteristic temperatures (*T<sub>i</sub>*, *T<sub>m</sub>* and *T<sub>f</sub>*) for the catalytic soot combustion over LaCuO-*x* (*x* = 500, 650 and 800).

Catalyst	<i>T<sub>i</sub></i> (°C) <sup>a</sup>	<i>T<sub>m</sub></i> (°C) <sup>a</sup>	<i>T<sub>f</sub></i> (°C) <sup>a</sup>
LaCuO-500	308	356	396
LaCuO-650	345	401	447
LaCuO-800	391	447	473

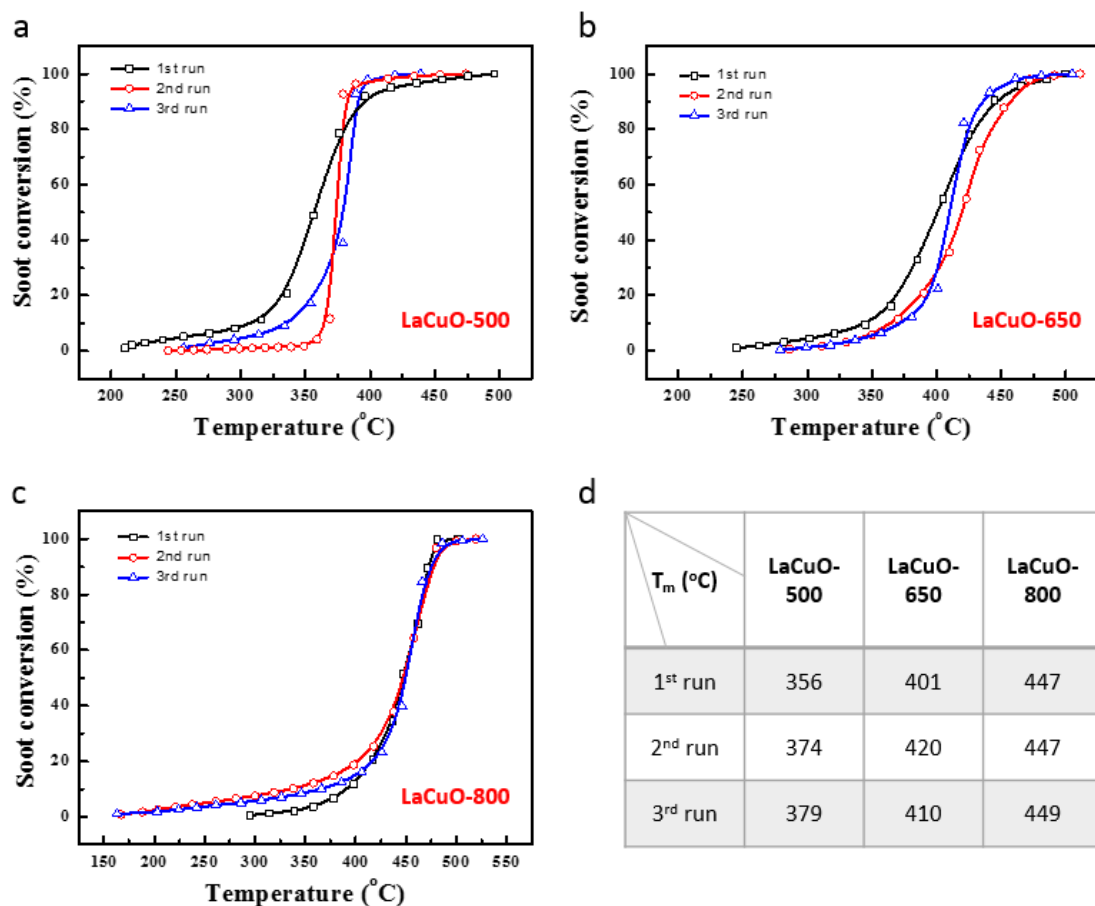
<sup>a</sup> derived from data in Fig. 1b.



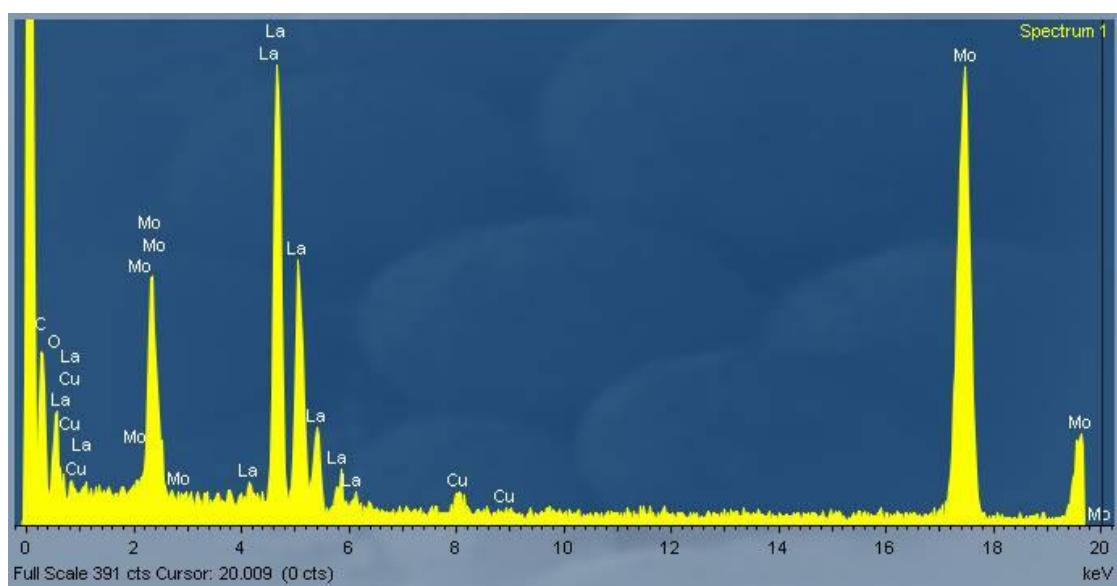
**Fig. S2.** Selectivity to CO<sub>2</sub> formation ( $S_{CO_2}$ ) with increasing temperature for catalytic soot combustion over LaCuO- $x$  ( $x = 500, 650$  and  $800$ ).  $S_{CO_2}$  here is defined as  $Conc_T(CO_2)/Conc_T(CO + CO_2)$ , where  $Conc_T(CO_x)$  is the outlet concentration of CO <sub>$x$</sub>  at temperature T. Conditions: 10 vol % O<sub>2</sub>, 350 ppmv NO, and N<sub>2</sub> in total flow of 200 sccm, soot/catalyst/silica: 10/100/1000 mg, temperature ramp rate: 5 °C/min.



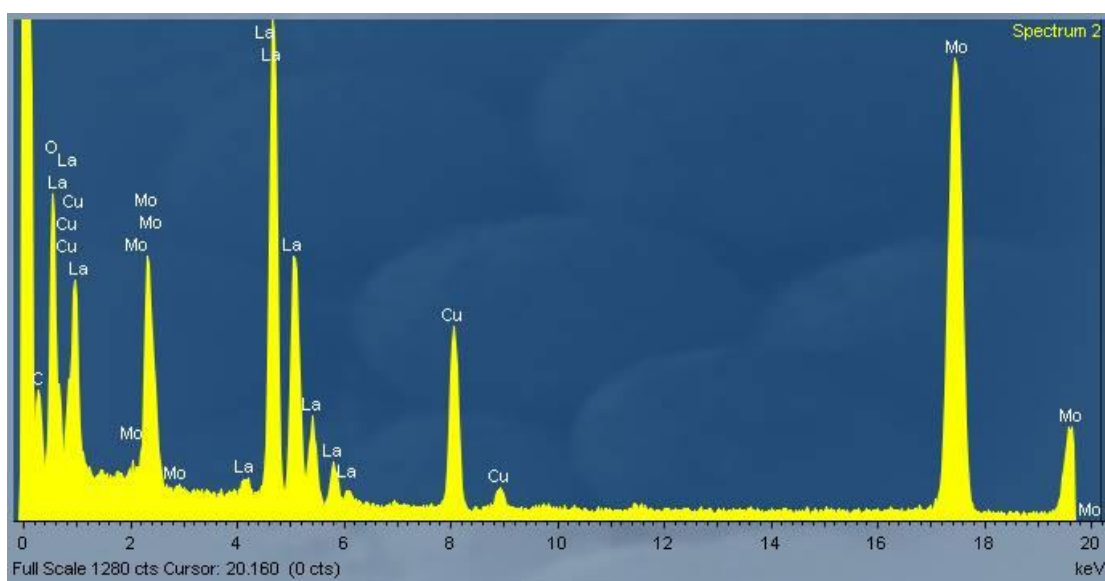
**Fig. S3.** Reaction between soot and water vapor ( $C-C^*+H_2O=C+CO+H_2$ , C\* refers to active site on soot surface). Condition: soot/silica: 10/1000 mg, N<sub>2</sub>: 552 sccm, H<sub>2</sub>O (g) content: 8%, total flow = 600 sccm. For reference (without soot), the condition is as follows: 1000 mg of silica, 552 sccm of N<sub>2</sub>, 8% H<sub>2</sub>O (g), total flow = 600 sccm. (The CO concentration was tested by an IR gas sensor (MultiGas™ 2030 FTIR Continuous Gas Analyzer), where the installed data processing procedure could turn the IR signal into gas concentration data.)



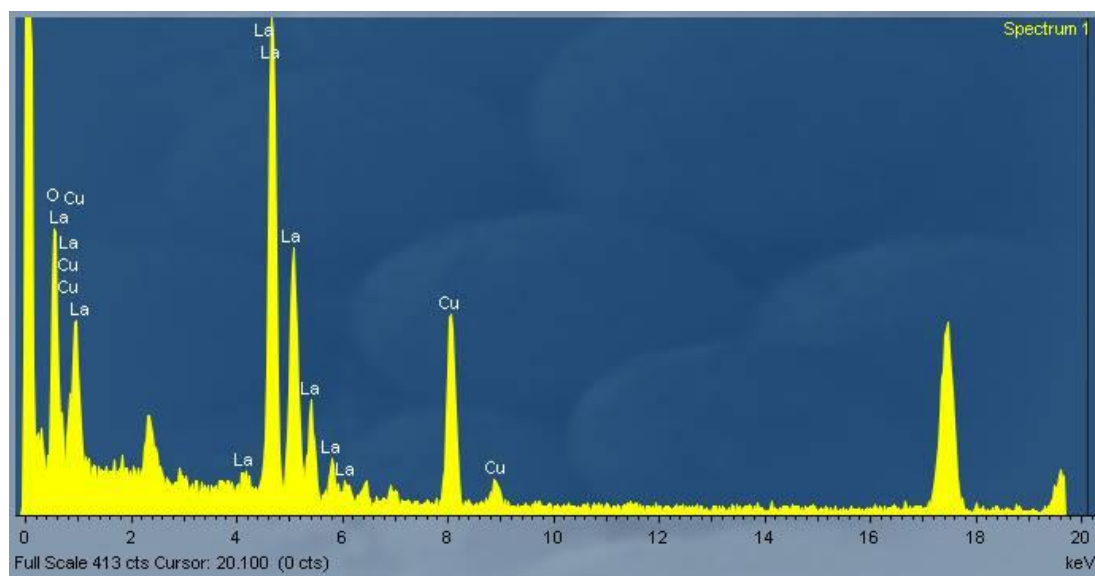
**Fig. S4.** Three repeated test runs of soot combustion over (a) LaCuO-500, (b) LaCuO-650 and (c) LaCuO-800. (d) Comparison of  $T_m$  values among the three repeated test runs for LaCuO- $x$  ( $x = 500, 650$  and  $800$ ). Conditions: For each run, the adopted conditions were identical to those in Fig. S2; while, after each run, 10 mg of soot was reloaded and mixed with the spent catalyst and silica.



**Fig. S5.** The TEM-EDS pattern of LaCuO-650 at site 1 shown in Fig. 4b.



**Fig. S6.** The TEM-EDS pattern of LaCuO-650 at site 2 shown in Fig. 4b.



**Fig. S7.** The TEM-EDS pattern of LaCuO-800.

**Table S2.** Chemical compositions of different samples or sites by TEM-EDS.

Elements	LaCuO-650 site 1			LaCuO-650 site 2			LaCuO-800		
	La	Cu	O	La	Cu	O	La	Cu	O
Atomic ratios (%)	61.67	2.74	35.59	34.54	13.25	52.21	35.86	14.50	49.65

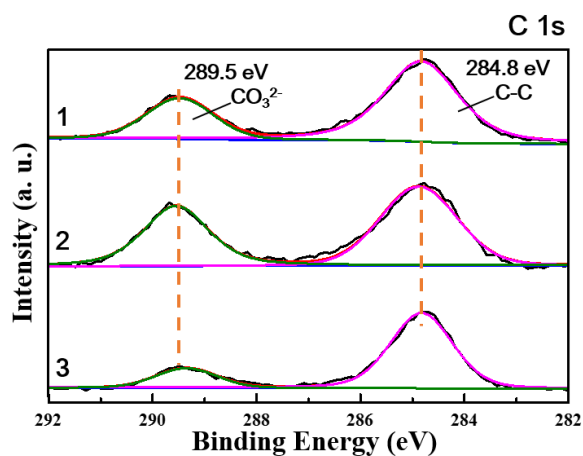


Fig. S8. C 1s XPS spectra of 1 (LaCuO-500), 2 (LaCuO-650), and 3 (LaCuO-800).

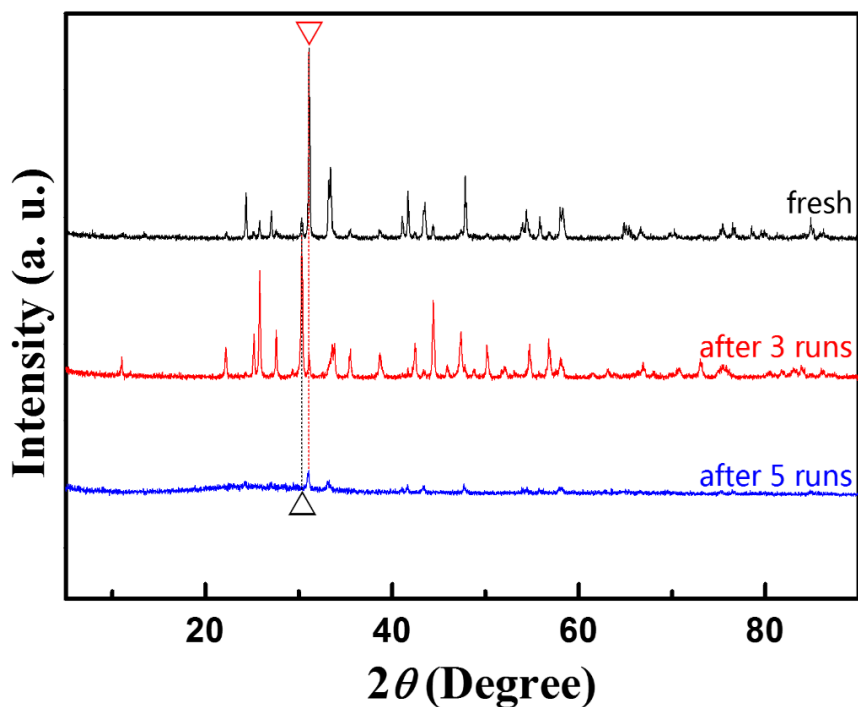


Fig. S9. XRD patterns of LaCuO-650 before (0) and after 3 or 5 runs of catalytic soot combustion test. Conditions: identical to that in Fig. S2.  $\triangle$ :  $\text{La}_2\text{O}_2\text{CO}_3$  JCPDF No.37-0804,  $\nabla$ :  $\text{La}_2\text{CuO}_4$  JCPDF No.27-1129. Note that the pattern for the sample after 5 runs of test (blue line) is weak (due to an inevitable loss of catalyst mass) but still strong enough to identify the main phase.

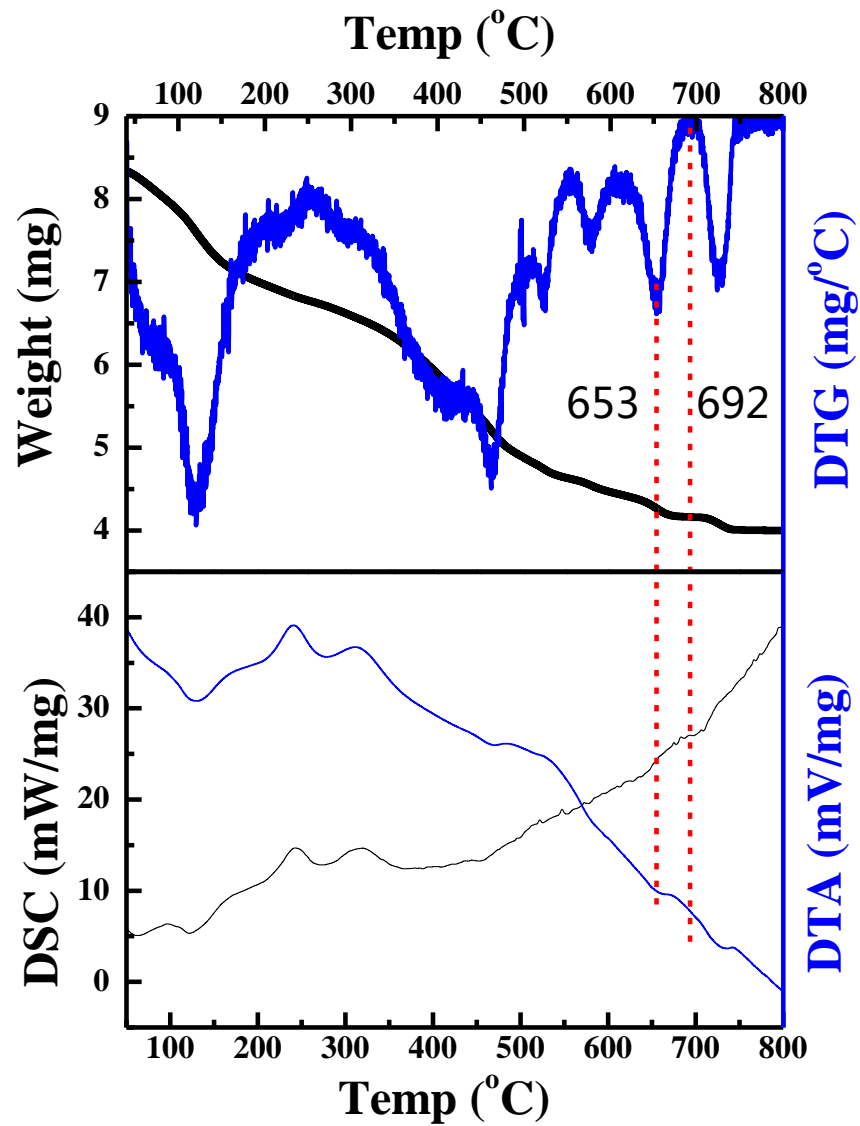
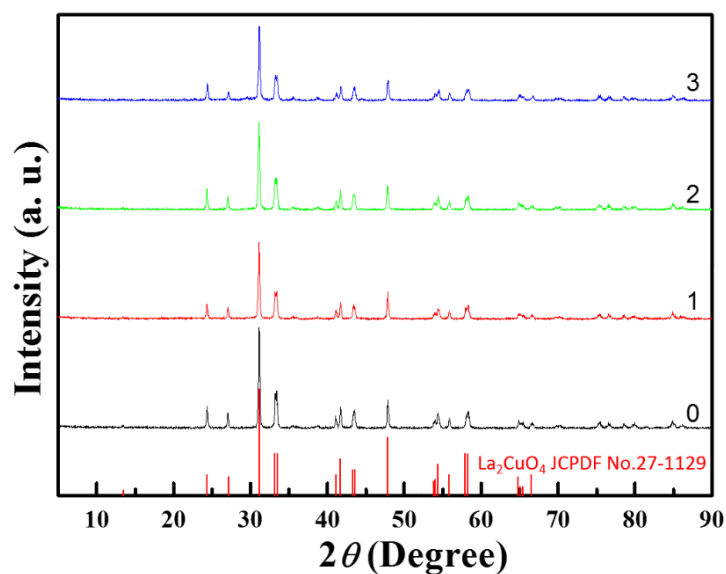
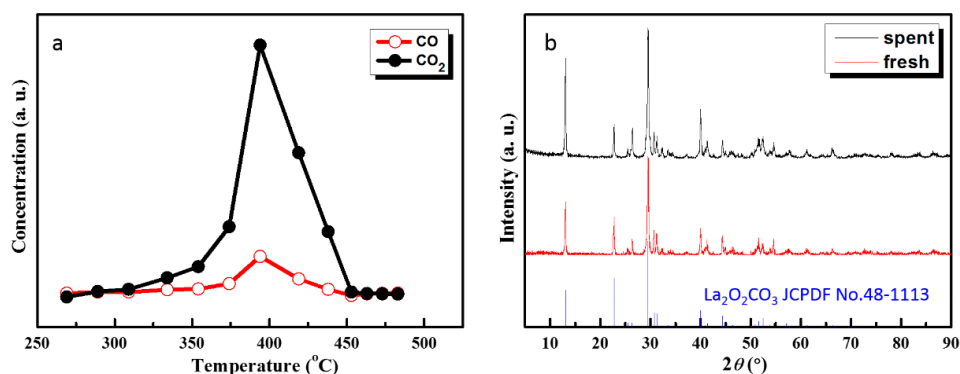


Fig. S10. Thermal analysis of the precursor for LaCuO-x.



**Fig. S11.** XRD patterns of LaCuO-690 before (0) and after 1-3 runs of catalytic soot combustion tests. Conditions: identical to that in Fig. S2. (Weak peaks centered around 35-40° assigned to CuO phase could also be seen.)



**Fig. S12.** (a) De-Soot (or catalytic soot combustion) activity of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. (b) Comparison of phase composition for La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> before and after De-Soot test. Conditions: identical to that in Fig. S2.

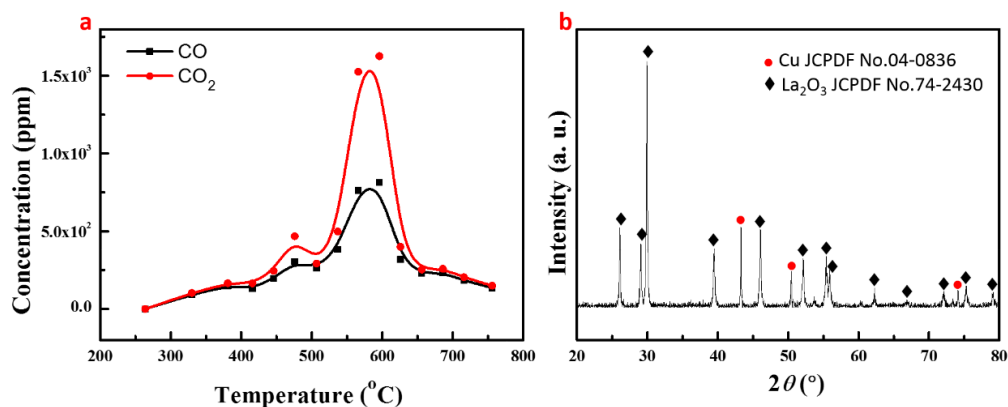
**Table S3.** Comparison of Selectivity for CO formation (Selectivity(CO)) during catalytic soot combustion over LaCuO-*x* (*x* = 500, 650 and 800) and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>.

Sample	LaCuO-500	LaCuO-650	LaCuO-800	La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>
Selectivity(CO)	12.5% <sup>a</sup>	16.5% <sup>a</sup>	9.8% <sup>a</sup>	20.6% <sup>b</sup>

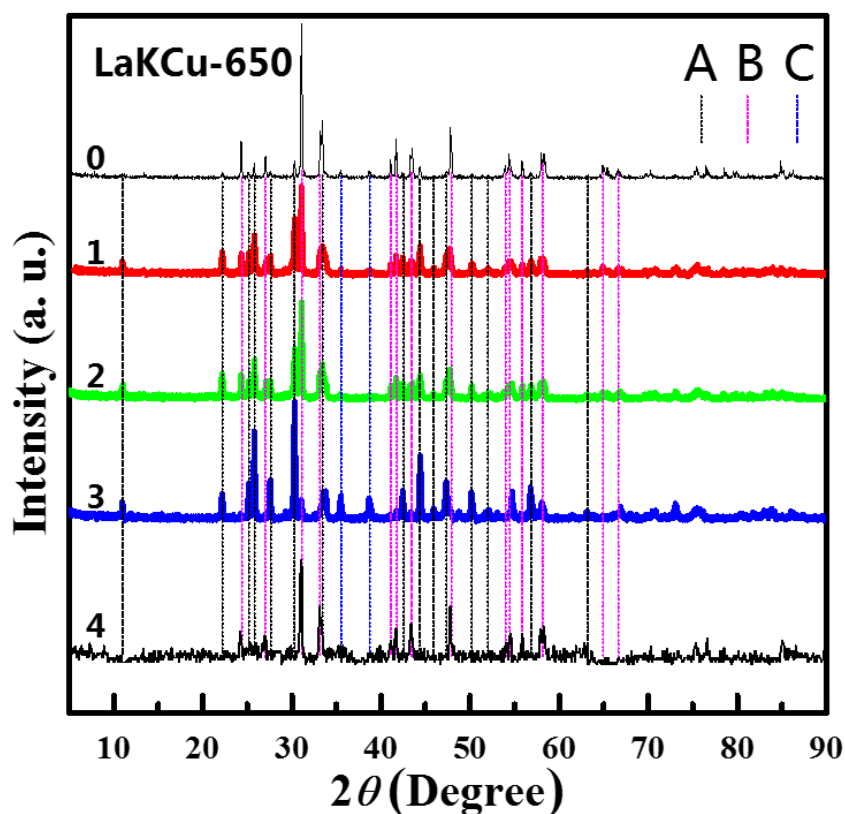
<sup>a</sup> Derived from data in Fig. 1a.

<sup>b</sup> Derived from data in Fig. S12.

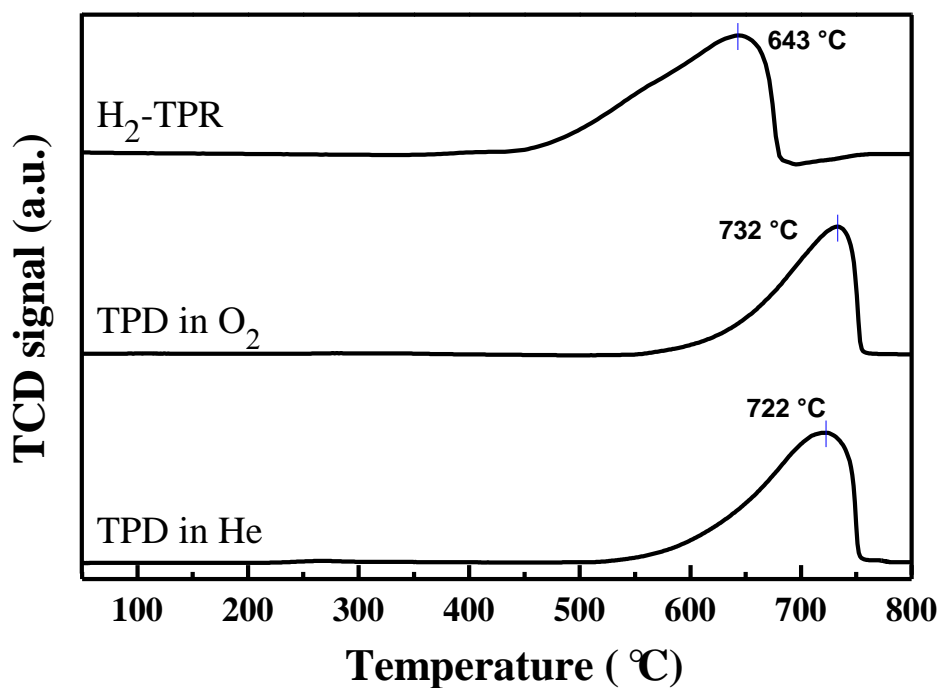




**Fig. S13.** (a) Variation of CO<sub>x</sub> ( $x = 1, 2$ ) concentration during soot-TPR for LaCuO-800. (b) XRD pattern of the product after soot-TPR test. Conditions: N<sub>2</sub>, 200 sccm, soot/sample/silica: 1000/100/1000 mg, temperature ramp rate: 5 °C/min.



**Fig. S14.** Comparison of XRD patterns for LaCuO-650 before (0) and after 1-4 runs of catalytic soot combustion tests. Note: For 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> runs, test temperature is below 500 °C, while for the 4<sup>th</sup> run, test temperature reached and was kept at 800 °C for 0.5 h. Conditions: identical to that in Fig. S2. (A-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, JCPDF No.37-0804; B-La<sub>2</sub>CuO<sub>4</sub>, JCPDF No.27-1129; C-CuO, JCPDF No.48-1548)



**Fig. S15.**  $\text{H}_2$ -TPR and TPD curves in  $\text{O}_2$  or He for  $\text{La}_2\text{O}_2\text{CO}_3$ . Conditions: For  $\text{H}_2$ -TPR, 10%  $\text{H}_2$  in Ar was fed at 200 mL/min; for TPD in  $\text{O}_2$ , 20%  $\text{O}_2$  in He was fed at 200 mL/min; and for TPD in He, pure He was fed at 200 mL/min. For all, the temperature was increased at 5  $^{\circ}\text{C}/\text{min}$ , and the sample was weighted as 100 mg.