## **Electronic Supporting Information**

## Modulating the active phase in perovskite LaCoO3 with B-

## site doping of Cu for efficient methanol reforming to

## produce hydrogen

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 $\label{eq:Fig.S1} Fig.S1 \ SEM \ images \ of \ (a) LaCoO_{3} \ (b) LaCo_{0.97} Cu_{0.03} O_{3} \ (c) LaCo_{0.94} Cu_{0.06} O_{3} \ (d) LaCo_{0.88} Cu_{0.12} O_{3} \ (d) LaCo_{0.88} Cu_{0.88} Cu_{0.88} \ (d) LaCo_{0.88} \ (d) LaCo_$ 







Fig.S3 (a) O 1s, (b) Co 2p, (c) Cu 2p, and (d)Cu LMM XPS spectra of LaCo<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub>-300 catalysts (A: x=0, B: x=0.03, C:x=0.06, D:x=0.12).



Fig.S4 XRD pattern of  $LaCo_{1-x}Cu_xO_3$  catalysts.



Fig.S5 The stability and cyclicity experiments of  $LaCo_{0.97}Cu_{0.03}O_3\mbox{-}300\ catalysts.$ 

Element Line	Weight %	Weight % Error	Norm. Wt.%	Norm. Wt.% Err	Atom %	Atom % Error
о к	15.10	± 0.13	15.10	± 0.13	53.26	± 0.45
Со К	20.71	± 0.13	20.71	± 0.13	19.83	± 0.12
Cu K	1.74	± 0.11	1.74	± 0.11	1.54	± 0.10
La L	62.45	± 0.31	62.45	± 0.31	25.37	± 0.13
Total	100.00		100.00		100.00	

Table S1 EDS results of LaCo<sub>0.97</sub>Cu<sub>0.03</sub>O<sub>3</sub>-300

Table S2 Chemical state distribution of elements on catalyst surface (Atomic %)

Complex	Cu		0			Со	
Samples	Cu <sup>1+</sup> (%)	Cu <sup>2+</sup> (%)	O <sub>1</sub> (%)	O <sub>II</sub> (%)	O <sub>Ⅲ</sub> (%)	Co <sup>3+</sup> (%)	Co <sup>2+</sup> (%)
LaCoO <sub>3</sub> -300			43.29	53.06	3.66	82.02	17.98
LaCo <sub>0.97</sub> Cu <sub>0.03</sub> O <sub>3</sub> -300	36.59	63.41	40.2	59.11	0.69	79.64	20.36
LaCo <sub>0.94</sub> Cu <sub>0.06</sub> O <sub>3</sub> -300	39.18	60.82	38.1	59.24	2.65	78.97	21.03
LaCo <sub>0.88</sub> Cu <sub>0.12</sub> O <sub>3</sub> -300	59.41	40.59	35.76	64.07	0.16	77.14	22.86