Electronic Supplementary Information

Facile Synthesis of Nanostructured Perovskites by

Precursor Accumulation on Nanocarbons

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A-site		B-site		solvent	Carbon	Drying temp.	Calcination
precursor	concentration (M)	precursor	concentration (M)	sontent	Curbon	(°C)	temp. (°C)
La(NO ₃) ₃ ·6H ₂ O	0.15	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	EtOH	KB	R.T.	600
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Co(NO_3)_2 \cdot 6H_2O$	0.15	EtOH	KB	130	600
$La(NO_3)_3 \cdot 6H_2O$	0.15	Fe(NO ₃) ₃ ·9H ₂ O	0.15	EtOH	KB	130	650
$La(NO_3)_3 \cdot 6H_2O$	0.15	Ni(NO ₃) ₂ ·6H ₂ O	0.15	EtOH	KB	130	750
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Al(NO_3)_3 \cdot 9H_2O$	0.15	EtOH	KB	130	800
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Ga(NO_3)_3 \cdot nH_2O$	0.15	EtOH	KB	130	850
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Cu(NO_3)_2 \cdot 3H_2O$	0.075	EtOH	KB	130	700
$Ca(CH_3COO)_2 \cdot H_2O$	0.15	Mn(CH ₃ COO) ₂ ·4H ₂ O	0.15	$\rm H_2O$	KB ^{a)}	130	850
$Ca(NO_3)_2 \cdot 4H_2O$	0.15	Fe(NO ₃) ₃ ·9H ₂ O	0.15	EtOH	KB	130	650
Ba(CH ₃ COO) ₂	0.15	Mn(CH ₃ COO) ₂ ·4H ₂ O	0.15	H_2O	KB ^{a)}	130	700
$Sr(CH_3COO)_2 \cdot 0.5H_2OO$	0.15	Mn(CH ₃ COO) ₂ ·4H ₂ O	0.15	H_2O	KB ^{a)}	130	700
La(NO ₃) ₃ ·6H ₂ O	0.105		0.15	ЦО	KD a)	120	(50
+ Sr(NO ₃) ₂	0.045	$Fe(NO_3)_3 \cdot 9H_2O$	0.15	H_2O	KB /	130	630
La(NO ₃) ₃ ·6H ₂ O	0.15	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	EtOH	CNF	R.T.	650
$La(NO_3)_3 \cdot 6H_2O$	0.15	Fe(NO ₃) ₃ ·9H ₂ O	0.15	EtOH	CNF	R.T.	650
$La(NO_3)_3 \cdot 6H_2O$	0.15	Ni(NO ₃) ₂ ·6H ₂ O	0.15	EtOH	CNF	130	750
$La(NO_3)_3 \cdot 6H_2O$	0.15	Al(NO ₃) ₃ ·9H ₂ O	0.15	EtOH	CNF	130	800
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Cu(NO_3)_2 \cdot 3H_2O$	0.075	EtOH	CNF	130	700
$Ca(NO_3)_2 \cdot 4H_2O$	0.15	Fe(NO ₃) ₃ ·9H ₂ O	0.15	EtOH	CNF	130	650
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	EtOH	KB	R.T.	520~560
$La(NO_3)_3 \cdot 6H_2O$	0.15	-	-	EtOH	KB	R.T.	520
-	-	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	EtOH	KB	R.T.	520
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	EtOH	absent	R.T.	650
$La(NO_3)_3 \cdot 6H_2O$	0.15	$Fe(NO_3)_3 \cdot 9H_2O$	0.15	EtOH	absent	R.T.	650
$La(NO_3)_3 \cdot 6H_2O$	0.15	Ni(NO ₃) ₂ ·6H ₂ O	0.15	EtOH	absent	R.T.	650
Sr(CH ₃ COO) ₂ ·0.5H ₂ O	0.15	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	$\rm H_2O$	absent	R.T.	650
Ba(CH ₃ COO) ₂	0.15	$Mn(NO_3)_2 \cdot 6H_2O$	0.15	H ₂ O	absent	R.T.	650

 Table S1 Preparation conditions of PA methods.

^{a)} KB was calcined at 773 K for 4 h to enhance the wettability of KB to water.

Perovskites	Specific surface area (m^2g^{-1})	Preparation method	Reference
LaFeO ₃	36	PA method	this work
LaFeO ₃	26	Sol-gel auto-combustion method	[1]
LaFeO ₃	15	Combustion synthesis method	[2]
LaNiO ₃	7	PA method	this work
LaNiO ₃	15	Sol-gel combustion technique.	[3]
LaNiO ₃	7	Citrate method	[4]
La_2CuO_4	4	PA method	this work
La_2CuO_4	46	PMMA templating and citric acid complexing method	[5]
LaAlO ₃	24	PA method	this work
LaAlO ₃	21	Pyrolysis of complex compounds with triethanolamine	[6]
LaGaO ₃	4	PA method	this work
LaGaO ₃	2	Pechini method	[7]
$La_{0.7}Sr_{0.3}FeO_3$	33	PA method	this work
$La_{0.7}Sr_{0.3}FeO_3$	7	Pechini method	[8]
$CaMnO_3$	5	PA method	this work
$CaMnO_3$	32	Citric acid assisted sol-gel method	[9]
$Ca_2Fe_2O_5$	32	PA method	this work
$Ca_2Fe_2O_5$	60	Citric acid assisted sol-gel method	[10]
$BaMnO_3$	9	PA method	this work
$BaMnO_3$	2	Sol-gel method using glycol and citric acid	[11]
SrMnO ₃	10	PA method	this work
SrMnO ₃	2	Sol-gel self-combustion method	[12]

Table S2 Comparison of specific surface area of perovskites prepared by the PA method to previous studies.

[1] Parida, K. M.; Reddy, K. H.; Martha, S.; Das, D. P.; Biswal, N., Fabrication of nanocrystalline LaFeO₃: An efficient sol-gel auto-combustion assisted visible light responsive. *Int. J. Hydrog. Energy.* **2010**, *35*, 12161-12168.

[2] Fino, D.; Russo, N.; Saracco, G.; Speechia, V., The role of suprafacial oxygen in some perovskites for the catalytic combustion of soot. *J. Catal.* **2003**, *217*, 367-375.

[3] Li, Y. Y.; Yao, S. S.; Wen, W.; Xue, L. H.; Yan, Y. W., Sol-gel combustion synthesis and visible-light-driven photocatalytic property of perovskite LaNiO₃. *J. Alloy Compd.* **2010**, *491*, 560-564.

[4] Rivas, M. E.; Fierro, J. L. G.; Guil-Lopez, R.; Pena, M. A.; La Parola, V.; Goldwasser, M. R., Preparation and characterization of nickel-based mixed-oxides and their performance for catalytic methane decomposition. *Catal. Today* **2008**, *133*, 367-373.

[5] Yuan, J.; Dai, H. X.; Zhang, L.; Deng, J. G.; Liu, Y. X.; Zhang, H.; Jiang, H. Y.; He, H., PMMA-templating preparation and catalytic properties of high-surface-area three-dimensional macroporous La₂CuO₄ for methane combustion. *Catal. Today* **2011**, *175*, 209-215.

[6] Ran, S.; Gao, L., Synthesis of LaAlO₃ powder using triethanolamine. Ceram. Int. 2008, 34, 443-446.

[7] Kumar, M.; Srikanth, S.; Ravikumar, B.; Alex, T. C.; Das, S. K., Synthesis of pure and Sr-doped LaGaO₃, LaFeO₃ and LaCoO₃ and SrMg-doped LaGaO₃ for ITSOFC application using different wet chemical routes. *Mater. Chem. Phys.* 2009, *113*, 803-815.

[8] Zhang, R. J.; Cao, Y.; Li, H. B.; Zhao, Z. L.; Zhao, K.; Jiang, L. Q., The role of CuO modified La_{0.7}Sr_{0.3}FeO₃ perovskite on intermediate-temperature partial oxidation of methane via chemical looping scheme. *Int. J. Hydrog. Energy* **2020**, *45*, 4073-4083

[9] Han, X. P.; Hu, Y. X.; Yang, J. G.; Cheng, F. Y.; Chen, J., Porous perovskite CaMnO₃ as an electrocatalyst for rechargeable Li-O₂ batteries. *Chem. Commun.* **2014**, *50*, 1497-1499.

[10] Sun, Z.; Chen, S. Y.; Hu, J.; Chen, A. M.; Rony, A. H.; Russell, C. K.; Xiang, W. G.; Fan, M. H.; Dyar, M. D.; Dklute, E. C., Ca₂Fe₂O₅: A promising oxygen carrier for CO/CH₄ conversion and almost-pure H₂ production with inherent CO₂ capture over a two-step chemical looping hydrogen generation process. *Appl. Energy* 2018, *211*, 431-442.
[11] Xu, W. T.; Shi, N.; You, Z. M.; Cai, J. J.; Peng, K.; Su, Z. M.; Zhou, J. C., Low-temperature NO decomposition through microwave catalysis on BaMnO₃-based catalysts under excess oxygen: Effect of A-site substitution by Ca, K and La. *Fuel Process. Technol.* 2017, *167*, 205-214.

[12] Rezlescu, N.; Rezlescu, E.; Popa, P. D.; Doroftei, C. L.; Ignat, M., Some nanograined ferrites and perovskites for catalytic combustion of acetone at low temperature. *Ceram. Int.* **2015**, *41*, 4430-4437.

perovskite	Crystallite size (nm)	Specific surface area (m ² g ⁻¹)
LaMnO ₃	14	21
LaFeO ₃	20	39
LaNiO ₃	16	6
LaAlO ₃	32	11
La_2CuO_4	58	2
$Ca_2Fe_2O_5$	31	25

 Table S3 Physicochemical properties of the perovskites using CNFs. Crystallite sizes were evaluated from XRD patterns using Scherrer's equation.

Table S4 Comparison for specific surface area of samples prepared with or without nanocarbons.

	Specific surface area (m ² g ⁻¹)		
	without C	with KB	
La + Mn	16	44	
La + Fe	8	36	
La + Ni	5	7	
Sr + Mn	9	10	
Ba + Mn	5	9	



Fig. S1 Nitrogen adsorption/desorption isotherm for LaMnO₃.



Fig. S2 SEM images of perovskites formed by the PA method using KB as carbon sources.



Fig. S3 SEM images of (a) CNFs and (b-f) perovskites formed by the PA method using CNFs as carbon sources.



Fig. S4 XRD patterns of perovskites formed by the PA method using CNFs as carbon sources.



Fig. S5 TEM images of LaMnO₃. Concentration of La(NO₃)₃·6H₂O and Mn(NO₃)₂·6H₂O: 0.01 M, solvent: ethanol, carbon: KB, drying temp.: 403 K, calcination temp.: 873 K.



Fig. S6 XRD patterns of the samples prepared by the calcination of metal salts without carbons.



Fig. S7 SEM image of La/Mn sample prepared without carbons. The preparation condition was described in the experimental section.



Fig. S8 TG/DTA profile of KB and KB accumulated with precursors.



Fig. S9 TG profile of LaMnO₃ prepared by the calcination at 793 K.