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Supporting Information for

Thermochemical CO_2 Splitting Using Double Perovskite-Type $Ba_2Ca_{0.66}Nb_{1.34-x}Fe_xO_{6-\delta}$†

Suresh Mulmi,[a] Haomin Chen,[b] Azfar Hassan,[c] Jose F. Marco,[d] Frank J. Berry,[e] Farbod Sharif,[c] Peter R. Slater,[e] Edward P. L. Roberts,[c] Stefan Adams,[b] and Venkataraman Thangadurai*[a]

[a] *Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N-1N4, Canada*

[b] *Department of Materials Science and Engineering, National University of Singapore, Singapore*

[c] *Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N-1N4, Canada*

[d] *Instituto de Química Física "Rocasolano", Consejo Superior de Investigaciones Cientificas, Serrano 119, 28006 Madrid, Spain*

[e] *School of Chemistry, The University of Birmingham, Birmingham B15 2TT, United Kingdom*

*Corresponding author: Venkataraman Thangadurai; vthangad@ucalgary.ca; Tel.: +1(403)-210-8649

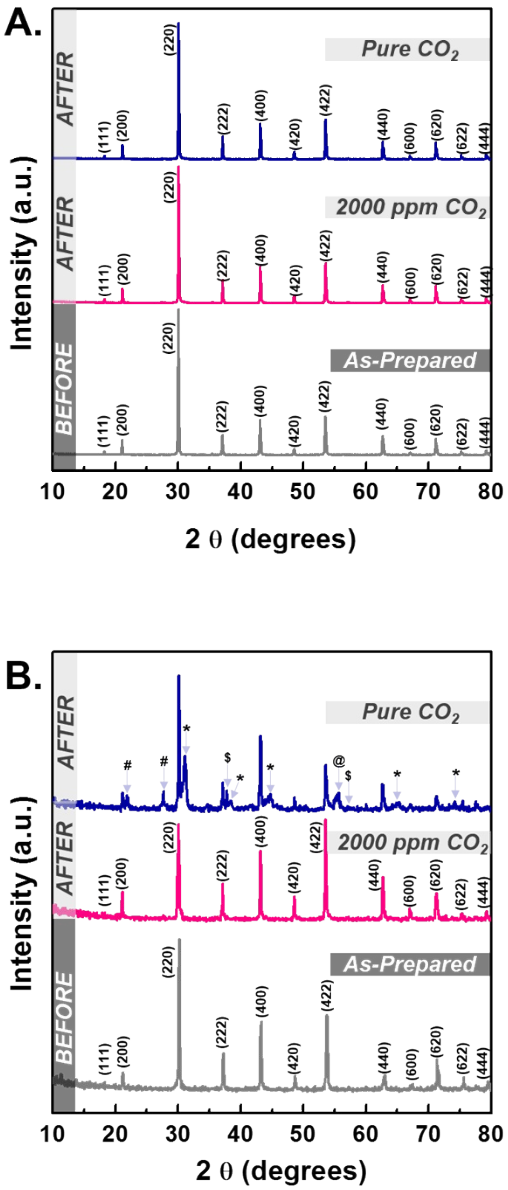
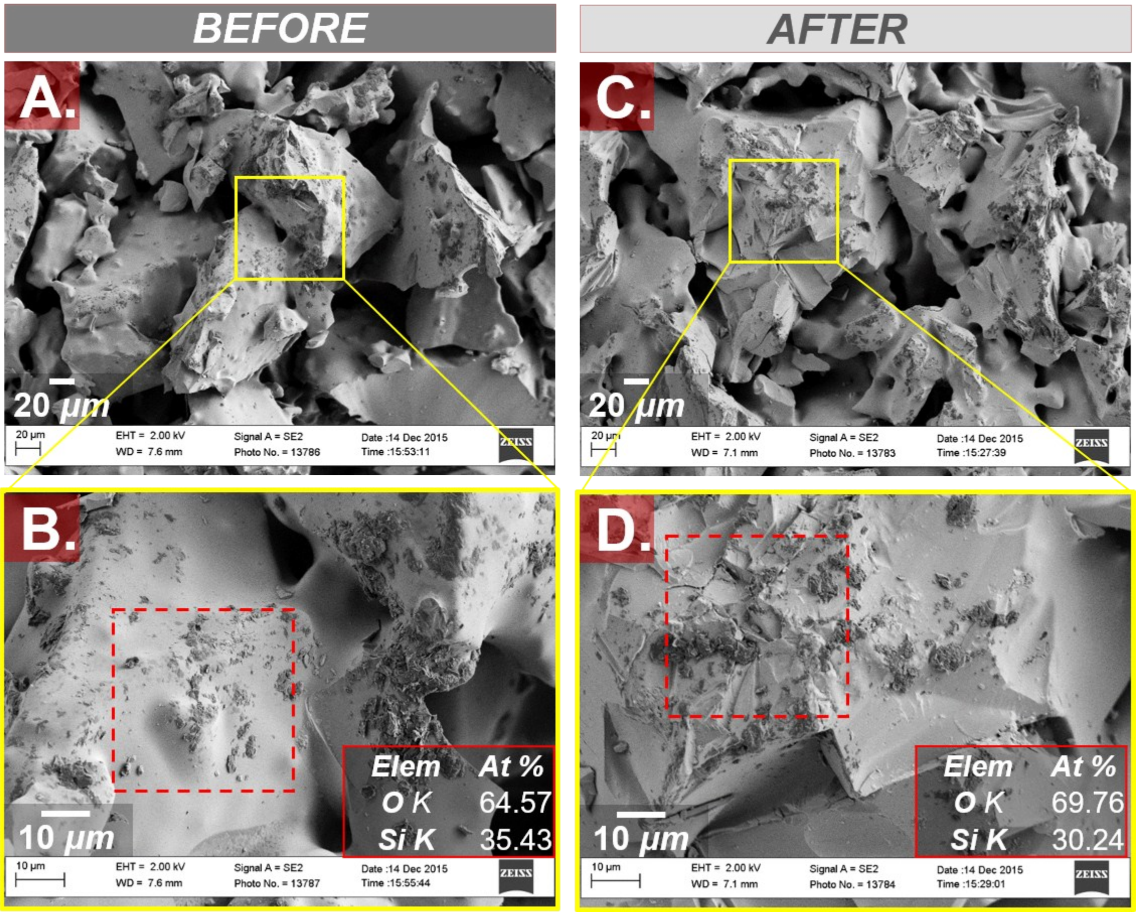


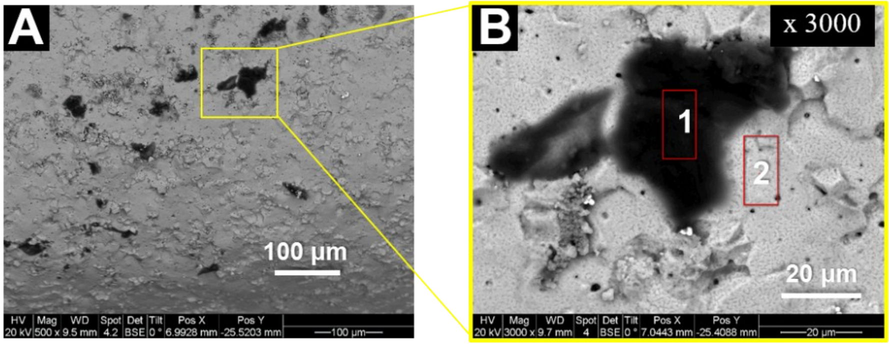
Figure S1. (A) PXRD patterns of as-prepared, 2000 ppm CO_2 (in Ar) and pure CO_2-treated BCNF66. (B) PXRD patterns of as-prepared, 2000 ppm CO_2 (in Ar) and pure CO_2-treated BCNF100. 2000 ppm CO_2 (in Ar) and pure CO_2 were continuously passed into quartz cell heated at 700 ^{o}C for 24 h at the flow rate of 100 sccm in two different experiments for each gaseous environment. The structure of BCNF100 was distorted after introducing pure CO_2 gas at elevated temperature. Symbols and corresponding JCPDS number of new impure diffraction patterns after CO_2-treatment in (B): # = $BaCO_3$ (05-0378); $ = Fe_2C (36-1249) @ = (26-1080), * = Fe_3O_4 (26-1136).



Elem	At %
O K	64.57
Si K	35.43

Elem	At %
O K	69.76
Si K	30.24

Figure S2. (A) Porous quartz glass before pure CO_2-treatment, (B) magnified view of (A); (C) porous quartz glass after pure CO_2-treatement, (D) magnified view of (C). EDX performed on selected area (with red-dotted lines) of (B) and (D) are shown on the figures, respectively.



EDX at Area 1 and 2

	1	2
Elem	At %	At %
C K	79.98	12.78
O K	12.93	51.51
NbL	1.23	6.91
CaK	1.20	5.79
BaL	3.58	18.49
FeK	1.07	5.98

Figure S3. Typical SEM images of BCNF66 pellets exposed to 3000 ppm CO_2 (bal. in Ar) for 24 h at 700 ^{o}C. (A) and (B) show the formation of carbon particles on the surface of the pellet at different magnifications when 100 mV dc voltage was applied using Au electrodes. “1” and “2” red boxes in (B) are the areas where EDX measurements were taken. EDX results of areas “1” and “2” are presented on the right side as a table.

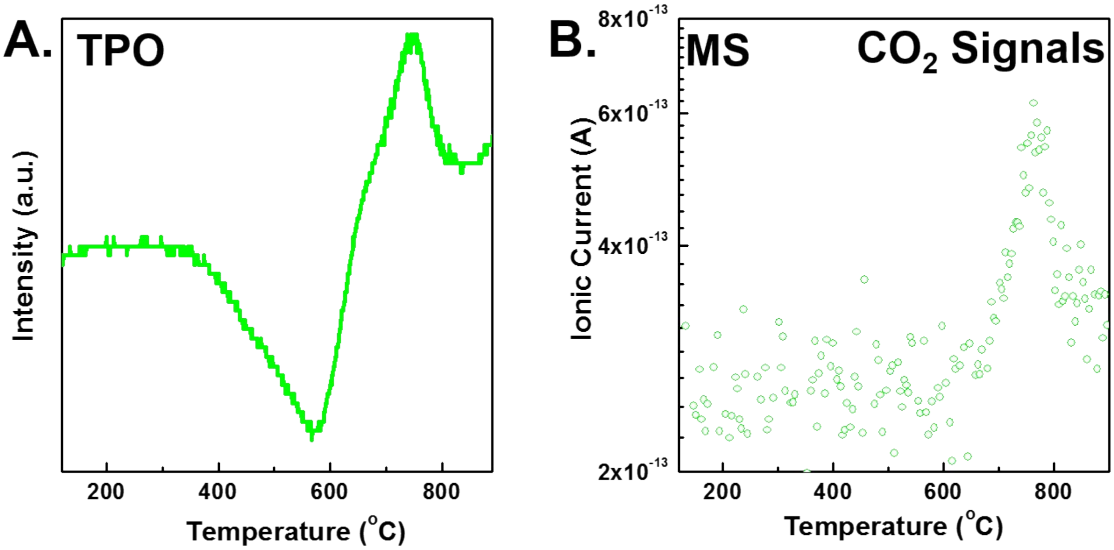
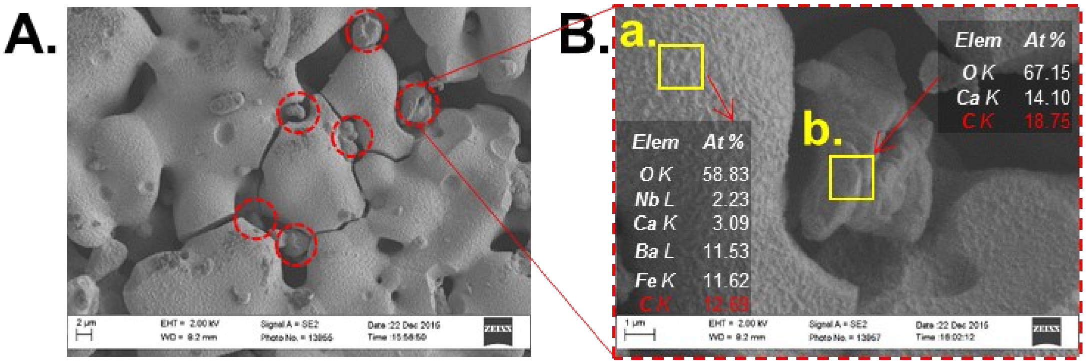


Figure S4. (A) Temperature programmed oxidation (TPO) profile of 0.3% CO_2 /Ar pre-treated (700 °C, 24h) $Ba_2(Ca_{0.66}Nb_{0.68}Fe_{0.66})O_{6-\delta}$ powder measured as a function of temperature using 5% O_2/ He (ramping rate = 10 °C/ min; total flow = 20 sccm) and (B) Corresponding mass spectra (MS) showing CO_2 signals.



Elem	At %
O K	58.83
Nb L	2.23
Ca K	3.09
Ba L	11.53
Fe K	11.62
C K	12.69

Elem	At %
O K	67.15
Ca K	14.10
C K	18.75

Figure S5. (A) Typical SEM image of BCNF100 pellet exposed to pure CO_2 for 24 h at 700 °C. Red circles in (A) shows the formation of new phase. (B) Magnified view of (A), where EDX is measured in (a) an area corresponding to parent phase and (b) is an area indicating new compound formed after CO_2 treatment.

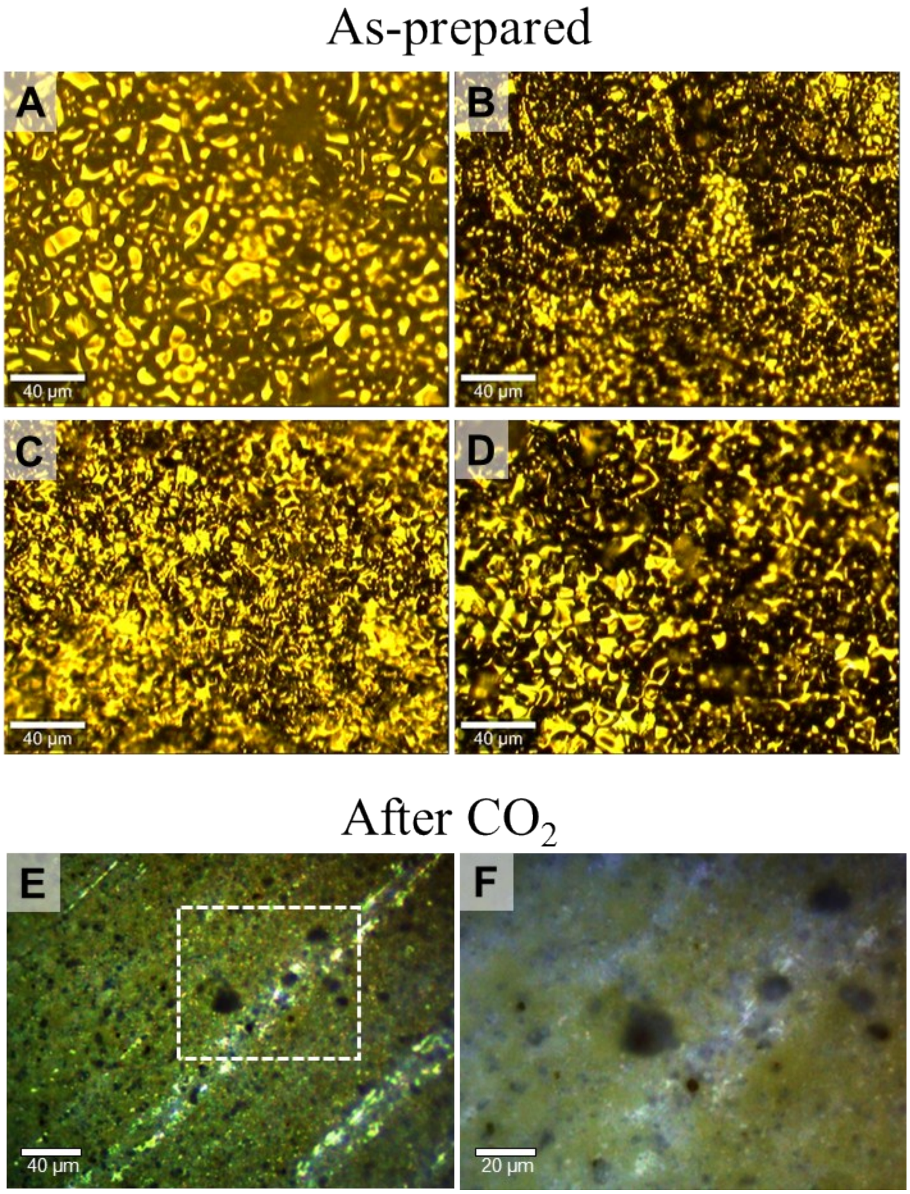


Figure S6. Images taken using Raman spectroscopy of as-prepared $Ba_2(Ca_{0.66}Nb_{1.34-x}Fe_x)O_{6-\delta}$ (BCNF) (A) x = 0, (B) x = 0.34, (C) x = 0.66, (D) x = 1, (E) CO_2-treated $Ba_2(Ca_{0.66}Nb_{0.68}Fe_{0.66})O_{6-\delta}$ sample (C), and (F) zoomed area of (E) shown dotted white square.

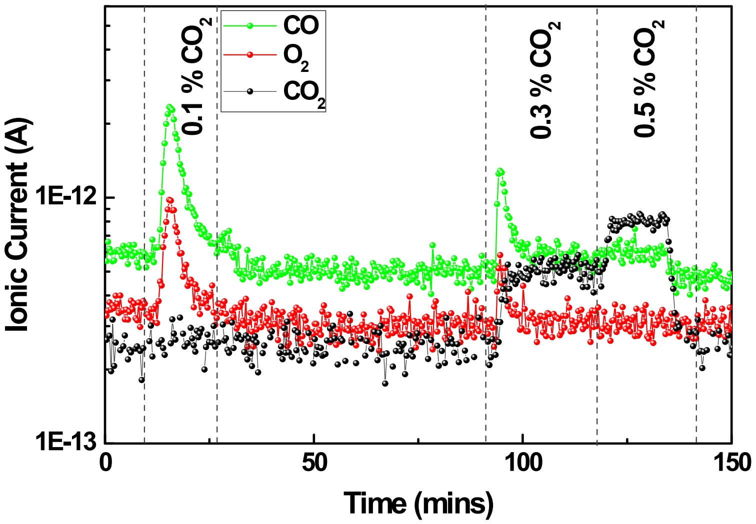


Figure S7. Mass spectra results showing the outcoming gaseous species using mass spectra for the CO_2 pre-treatment process in as-prepared BCNF66 at 700 °C. Gases used were Ar as base gas and CO_2 balanced in Ar. (Gas flow rate = 100 sccm).

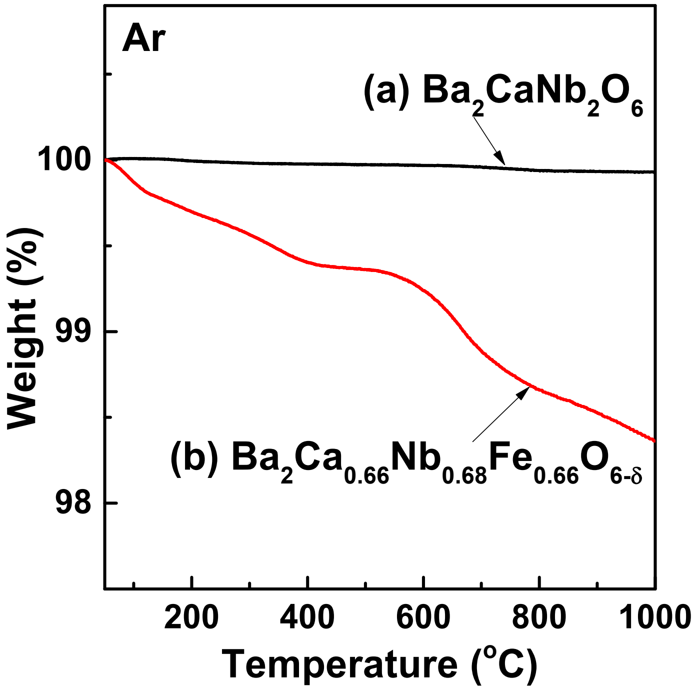


Figure S8. Thermal gravimetric analysis (TGA) of (a) BCN and (b) BCNF66 under Ar at heating rate of 5 °C/min.

Table S1. Impurities in BCNF100 after CO_2-treatment from PXRD diffraction patterns

Impurity	JCPDS Card No.	Lattice	Lattice parameters	Space group
$BaCO_3$	05-0378	Orthorhombic	*a* = 5.314 Å; *b* = 8.904; c = 6.43 Å	*Pmcn* (*No.* 62)
Fe_2C	36-1249	Hexagonal	*a* = *b* = 2.754 Å; c = 4.349 Å	*P63/mmc* (*No.* 194)
C	26-1080	Hexagonal	*a* = *b* = 2.456 Å; c = 13.392 Å	*P63mc* (*No.* 186)
Fe_3O_4	26-1136	Face-centered cubic	*a* = *b* = *c* = 8.0903 Å	*Fd-3m* (*No.* 227)

Table S2. ^{57}Fe Mössbauer parameters for materials of composition $Ba_2Ca_{0.66}Nb_{1.34-x}Fe_xO_{6-\delta}$

Sample $Ba_2Ca_{0.66}Nb_{1.34-x}Fe_xO_{6-x}$	Component	δ (mms^{-1}) +/- 0.02	Δ (mms^{-1}) +/-0.02	Γ (mms^{-1})	Area (%)
x = 0.33	Fe^{5+}	-0.08	0.77	0.50	50
	Fe^{4+}	0.06	--	0.24	3
	Fe^{3+}	0.15	1.48	0.42	47
x = 0.66	Fe^{5+}	-0.09	0.73	0.56	32
	Fe^{4+}	0.05	--	0.30	4
	Fe^{3+}	0.16	1.49	0.40	64
x = 0.66 CO_2-treated	Fe^{5+}	--	--	--	--
	Fe^{4+}	0.06	--	0.34	3
	Fe^{3+}	0.17	1.45	0.44	97
x = 1	Fe^{5+}	-0.08	0.77	0.48	12
	Fe^{4+}	0.04	--	0.44	7
	Fe^{3+}	0.15	1.52	0.46	81

Table S3. Relative energy of different surface compositions with surface F1 as a reference point. Negative energy indicates more stable configuration.

No.	Composition	Energy (eV/atom)	Remark
F1	2 Fe, 1 Nb, 1 Ca	0.000	Reference point
F2	1 Fe, 2 Nb, 1 Ca	0.003	
F3	0 Fe, 3 Nb, 1 Ca	0.004	
F4	3 Fe, 0 Nb, 1 Ca	-0.034	
F5	3 Fe, 1 Nb, 0 Ca	0.058	Surface heavily distorted
F6	4 Fe, 0 Nb, 1 Ca	---	Surface destroyed

Table S4. Formation energies of O-vacancy at concentration of 12.5% on different surface calculated from $Ba_{16}Ca_4Nb_7Fe_5O_{48}$ === $Ba_{16}Ca_4Nb_7Fe_5O_{47}$ + ½ O_2. Negative values indicate spontaneous formation.

No.	Surface	O vacancy between	Energy (eV)
D1	2 Fe, 1 Nb, 1 Ca	Fe and Nb	-0.845
D2	2 Fe, 1 Nb, 1 Ca	Fe and Ca	-0.798
D3	1 Fe, 2 Nb, 1 Ca	Fe and Nb	1.405
D4	1 Fe, 2 Nb, 1 Ca	Fe and Ca	0.042
D5	1 Fe, 2 Nb, 1 Ca	Nb and Ca	-0.519
D6	1 Fe, 2 Nb, 1 Ca	Nb and Nb	-0.514
D7	0 Fe, 3 Nb, 1 Ca	Nb and Ca	-0.491
D8	0 Fe, 3 Nb, 1 Ca	Nb and Nb	-0.370
D9	3 Fe, 0 Nb, 1 Ca	Fe and Fe	1.088