Supplementary information

Beneficial effects of substituting trivalent ions in the B-site of $La_{0.5}Sr_{0.5}Mn_{1-x}A_xO_3$ (A=Al, Ga, Sc) on the thermochemical generation of CO and H₂ from CO₂ and H₂O.

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S-A. Experimental Section:

1) Synthesis: The synthetic methods along with the precursors used and heating conditions are summarized in Table S1.All $La_{0.5}Sr_{0.5}Mn_{1-x}A_xO_3$ (A= Al, Ga and Sc) are prepared by modified Pecini route. Stoichiometric amounts of metal nitrate precursors were dissolved in water. Sc_2O_3 was converted to nitrate by heating in boiling HNO₃. EDTA (EDTA: metal cations molar ratio= 1:1) dissolved in aqueous ammonia, slowly added to metal ions solution with stirring, combined with citric acid (citric acid: metal cations molar ratio= 1:2) followed by excess addition of aqueous ammonia to make the final solution become transparent (final pH=10). The gel was formed at 80°C, followed by drying at 200°C for 12 hrs. The product was heated at 800°C and 1400°C for 10 hrs each.

2) Characterizations: Phase identification was carried out by PXRD analysis with a Bruker D8 Advance diffractometer applying Cu K α radiation. Lebail fitting was carried out using Fullprof software in order to obtain the cell parameters. FEI Nova Nanosem 600 was used to record the field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDS). BET measurements was carried out in Quanta-chrome Autosorb instrument at 77K from N₂ absorption.

3) Reactivity Tests: i) CO₂ Splitting Test: O₂ evolution and CO₂ splitting experiments were performed by thermo gravimetric analysis (TGA) using a Perkin-Elmer Pyris1 instrument. About 100 mg sample (pelletized) was introduced in a platinum crucible to place inside the furnace chamber. Sample was heated upto 1400°C with a ramp rate of 20°C/min and maintained for 45 mins in presence of continuous Ar (99.9999%) flow of 40 sccm. After cooling down to oxidation temperature (1100°C), 40% CO₂ mixed with Ar was injected to carry out CO₂ splitting experiment. The total amount of O₂ evolved and CO produced was registered by calculating the change in mass, as per the details shown in Equation S1 and S5 (ESI).

ii) Investigation of carbonate formation: In order to examine the carbonate formation using TGA, two experiments were performed. In the first experiment, after reduction at 1400°C (for 45 mins) sample was cooled down to 700°C. At 700°C, CO_2 (40% v/v in Ar) was introduced in the sample chamber and immediately the temperature is further ramped up to 1200°C (heating rate of 10°C/min) in presence of CO₂. In the second experiment, after reduction at 1400°C (for 45 mins) sample was cooled down to 850°C. At 850°C, CO_2 (40% v/v in Ar) was introduced in the sample chamber to carry out the oxidation for 1 hour. The temperature is further ramped up to 1200°C with a heating rate of 10°C/min in presence of Ar (see ref. 39 of main text for more experimental details).

iii) H_2O Splitting Test: The water splitting activity was investigated using an experimental set up described earlier (refs. 15 and 16 of main text). About 500 mg of the sample was placed in an alumina crucible and pushed inside a tubular furnace. The sample temperature was ramped upto 1400 °C (rate 10°C/min) and maintained under inert atmosphere until complete reduction happens. The furnace was cooled down to 1100°C and steam injected along with continuous flow of inert gas to perform the H₂ generation step. The detection and measurement of evolved

gases were carried out with a gas chromatograph (PerkinElmer Clarus ARNEL 580) equipped with a TCD detector. Numerical integration of molar flow rate-time curves gives the total amount of O₂ evolved whereas total amount of H₂ was calculated by the water displacement method.

S-B. Detailed calculations of TGA analysis:

The weight loss in TGA measurements is converted to the mole amount of O₂ produced/gram of composites by the following equation,

 $n_{O_2} = \Delta m_{loss} / \left[M_{O_2} \cdot m_{material} \right]$ (S1)

 Δm_{loss} is the mass loss registered by TGA during reduction, M_{0_2} is the molecular weight of O₂ and $m_{material}$ is the mass of compound investigated during the TGA experiment.

The calculation of Reduction yield ($% X_{red}$) are as follows,

 $% X_{red} = \frac{n_{0_2}/n_{0_2, \max \times 100}}{(S2)}$

 $n_{0_{2,max}} = x/4. M_{material}$ (S3) With

" χ " denotes the stoichiometric coefficient of "A" in Ln_{0.5}A_{0.5}MO₃ composition. ^Mmaterialis the molecular weight of specific Ln_{0.5}A_{0.5}MO₃ composition. The amount of CO produced (mol/g) is calculated as follows,

 $n_{CO} = \Delta m_{gain} / [M_0 \cdot M_{material}] \qquad -----(S4)$

 Δm_{gain} is the mass gain registered by TGA during CO₂ splitting experiment and M_0 is the atomic weight of O.

The oxidation yield ($\%\alpha$) is calculated as follows,

$$\alpha = \frac{\frac{n_{CO}}{X_{red} \times \frac{x}{2M_{material}}}} = \frac{n_{CO}}{2 \times n_{O_2}} \times 100$$
(S5)

S-C. Calculation of tolerance factor (τ)

In ABO₃ perovskite,

the Goldsmith tolerance factor (τ) is calculated as, $\tau = \frac{(r_A + r_0)}{\sqrt{2}(r_B + r_0)}$(S6)

here r_A , r_B and r_O denotes the ionic radii of the constituent ions. In the present study " τ " is

Composition	X	Precursors	Synthesis	Heating conditions
			method	

La _{0.5} Sr _{0.5} Mn _{1-x} Al _x O ₃	0,0.25, 0.35,0.5	La(NO ₃₎₃ ,6H ₂ O (Sigma- Aldrich),Sr(NO ₃) ₂ (Fluka), Al(NO ₃₎₃ ,6H ₂ O(Merck),, Mn(NO ₃) ₃ ,9H ₂ O(Merck)	Sol-Gel	80°C for 8hrs, 200°C for 12hrs, 800°C for 10hrs, 1400°C for10hrs
$La_{0.5}Sr_{0.5}Mn_{1-x}Ga_xO_3$	0.25,0.35,0 .5	La(NO ₃₎₃ ,6H ₂ O, Sr(NO ₃) ₂ , Ga(NO ₃₎₃ ,6H ₂ O(Merck), Mn(NO ₃) ₃ ,9H ₂ O	Sol-Gel	80°C for 8hrs, 200°C for 12hrs,800°C for 10 hrs, 1400°C for10hrs
La _{0.5} Sr _{0.5} Mn _{1-x} Sc _x O ₃	0.05,0.1, 0.15, 0.25	La(NO ₃₎₃ ,6H ₂ O, Sr(NO ₃) ₂ ,Sc ₂ O ₃ (Sigma- Aldrich), HNO ₃ (70%), Mn(NO ₃) ₃ ,9H ₂ O	Sol-Gel	80°C for 8hrs, 200°C for 12hrs,800°C for 6hrs, 1400°C for10hrs

calculated considering 12 and 6 coordination no. of A and B site cations respectively. ^[1, 2]

Table S1.Summary of the synthesis conditions of perovskites.



Fig. S1. PXRD patterns of $La_{0.5}Sr_{0.5}Mn_{0.5}Ga_{0.5}O_3$. Extra diffraction peaks are marked by (*) shows the presence of secondary phases beside the formation of main perovskite structure.



Fig. S2 (a) Full range and (b) magnified PXRD patterns of $La_{0.5}Sr_{0.5}Mn_{1-x}Sc_xO_3$ (x=0.15, 0.25). Diffraction peaks marked by (*) confirms the presence of Sc_2O_3 (2θ ~31.2°) beside the formation of main perovskite structure.



Fig. S3 (a) PXRD patterns and (b) magnified view of the (110) reflections of $La_{0.5}Sr_{0.5}Mn_{1-x}Al_xO_3$ (x=0.25, 0.35, 0.5). (c) Lebail fitted PXRD patterns of $La_{0.5}Sr_{0.5}Mn_{0.5}Al_{0.5}O_3$ (lattice parameters are in Table S2).



Fig. S4 Lebail fitted PXRD patterns of (a) $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ and (b) $La_{0.5}Sr_{0.5}Mn_{0.65}Ga_{0.35}O_3$ (lattice parameters are in Table S2).



Fig. S5 Lebail fitted PXRD patterns of (a) $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ and (b) $La_{0.5}Sr_{0.5}Mn_{0.9}Sc_{0.1}O_3$ (lattice parameters are in Table S2).

Table S2. Summary of Space group (S.G.) and tolerance factor (τ) and lattice parameters (obtained from LeBail fitting, see Figs. S3-S5) of La_{0.5}Sr_{0.5}Mn_{1-x}A_xO₃ (A=Al, Ga and Sc). Shanon radii of the corresponding cations are mentioned in parenthesis are as follows; Mn³⁺ (0.645Å), Mn⁴⁺ (0.53Å), Al³⁺(0.535Å), Ga³⁺(0.62Å), Sc³⁺(0.745Å), La³⁺(1.36Å), Sr²⁺(1.44Å), O²⁻(1.4Å).

La _{0.5} Sr _{0.5} Mn _{1-x} A _x O ₃	x	Tolerance factor (τ)	S. G.	a (Å)	b (Å)	c (Å)	Cell vol. (Å ³)
A=Al	x=0.25	1.01	R-3c	5.4409(7)	5.4409(7)	13.333(1)	341.83
	x=0.35	1.016	R-3c	5.3973(2)	5.3973(2)	13.2216(4)	333.56
	x=0.5	1.024	R-3c	5.3880(4)	5.3880(4)	13.2003(8)	331.87
A=Ga	x=0.25	0.999	R-3c	5.4592(3)	5.4592(3)	13.363(1)	344.92
	x=0.35	1.000	R-3c	5.4630(5)	5.4630(5)	13.330(2)	344.54
A=Sc	x=0.05	0.993	R-3c	5.4594(3)	5.4594(3)	13.3764(9)	345.3
	x=0.1	0.991	R-3c	5.4686(9)	5.4686(9)	13.393(2)	346.9





Fig. S6 (a)FESEM image and (b, c) EDX mapping of as synthesized La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O₃.

Fig. S7 (a)FESEM image and (b, c) EDX mapping of as synthesized La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O₃.



Fig. S8 (a) TGA plot and (b) corresponding histogram of $La_{0.5}Sr_{0.5}Mn_{0.5}Al_{0.5}O_3during three consecutive thermochemical CO₂ splitting cycles (reduction and oxidation temperature is 1400°C and 1100°C respectively).$





Fig. S9 FESEM images of $La_{0.5}Sr_{0.5}Mn_{0.5}Al_{0.5}O_3$ (a) before and (b) after TG analysis. EDS (X and Y axis are Energy in KeV and counts respectively) of the same (c) before and (d) after TGA.

Table S3. Atomic % of La, Sr, Al and Mn present in $La_{0.5}Sr_{0.5}Mn_{0.5}Al_{0.5}O_3$ before and after TG analysisas calculated from EDS analysis.

	La L	Sr L	Al K	Mn K	O K
$La_{0.5}Sr_{0.5}Mn_{0.5}Al_{0.5}O_{3}$	Atomic %				
Before TGA	11.6	11.7	12.8	11.1	52.8
After TGA	11.2	10.9	11.6	11.3	54.9



Fig. S10 Evolution of oxygen nonstoichiometry of $La_{0.5}Sr_{0.5}Mn_{1-x}Ga_xO_3$ (x= 0.25, 0.35) during TGA. Histogram depicts reduction (% X_{red}) and reoxidation yield (% α) at temperature 1400°C and 1100°C respectively



Fig. S11 Evolution of oxygen nonstoichiometry of $La_{0.5}Sr_{0.5}Mn_{1-x}Sc_xO_3(x=0.05, 0.1)$ during TGA. Histogram depicts reduction (% X_{red}) and reoxidation yield (% α) of the same. Reduction and oxidation temperature is 1400°C and 1100°C respectively.



Fig. S12 (a)TGA plot and (b) corresponding histogram for $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ during three consecutive thermochemical CO₂ splitting cycles (reduction and oxidation temperature is 1400°C and 1100°C respectively).



Fig. S13 (a)TGA plot and (b) corresponding histogram for $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ during three consecutive thermochemical CO₂ splitting cycles (reduction and oxidation temperature is 1400°C and 1100°C respectively).



Fig. S14 PXRD patterns of (a) $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ and (b) $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ before and after TGA.



Fig. S15 FESEM images of $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ (a) before and (b) after TG analysis and of $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ (c) before and (d) after TG analysis.



Fig. S16 EDS (X and Y axis are Energy in KeV and counts respectively) of $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ (a) before and (b) after TG analysis and of $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ (c) before and (d) after TG analysis respectively.

Table S4. Atomic % of La, Sr, Ga and Mn present in $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ before and after TG analysisas calculated from EDS analysis.

	La L	Sr L	Ga K	Mn K	O K
$La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_{3}$	Atomic %				
Before TGA	13.15	13.03	5.61	17.75	50.46
After TGA	13.27	12.48	5.95	18.11	50.18

Table S5. Atomic % of La, Sr, Sc and Mn present in $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ before and after TG analysis as calculated from EDS analysis.

	La L	Sr L	Sc K	Mn K	O K
$La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$	Atomic %				
Before TGA	12.9	13.8	1.69	24.9	46.7
After TGA	12.13	14.1	1.77	26.9	45.2



Fig. S17 (a) TG reduction of $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ (T_{red} =1400°C, Ar gas), followed by cooling at 700°C and subsequent temperature ramp from 700°C to 1200°C under CO₂ exposure (b) TG reduction of $La_{0.5}Sr_{0.5}Mn_{0.75}Ga_{0.25}O_3$ (T_{red} =1400°C, Ar gas), followed by CO₂ exposure at 850°C and further decomposition upto 1200°C under Ar (heating rate= 10°C/min). Red lines indicate the starting point of O₂ evolution during reduction under Ar. Experimental details are in section S-A-3(ii) of supporting information.



Fig. S18 (a) TG reduction of $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ ($T_{red}=1400^{\circ}C$, Ar gas), followed by cooling and temperature ramp from 700°C to 1200°C under CO₂ exposure (b) TG reduction of $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$ ($T_{red}=1400^{\circ}C$, Ar gas), followed by CO₂ exposure at 850°C and further decomposition upto 1200°C under Ar (heating rate= 10°C/min). Vertical lines indicate the starting point of O₂ evolution during reduction under Ar. Experimental details are in section S-A-3(ii) of supporting information.



Fig. S19 TGA curves of thermochemical CO_2 splitting of $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$. The weight gain (CO production) region is highlighted to show two different kinetics. Step 1 (yellow colour) shows the rapid gain of CO. Step 2 (grey colour) highlights the slow kinetics. CO_2 splitting temperature is 1100°C.

Table S6. CO production in two different kinetics by $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$

	CO produced (µmol/g)			
Material	CO produced (µmol/g) Fast kinetics(1)	CO produced (µmol/g) Slow kinetics (2)	Total CO produced (µmol/g)	
$La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_{3}$	<u>243</u>	300	543	

References:

- [1]R. D. Shannon, ActaCrystallogr. 1976, 32751.
- [2] http://abulafia.mt.ic.ac.uk/shannon/ptable.php