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Supporting information

Significant Reduction in the operating temperature of the Mn(II)/Mn(III) oxide-based thermochemical water splitting cycle brought about by the use of nanoparticles

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Experimental Section

Synthesis: Mn_3O_4 (97%, sigma) and Na_2CO_3 (99.5%, MERCK) were used as starting materials for ball milling. Around 1.5 gms of sample (Mn_3O_4/ Na_2CO_3) was ball milled in Fritsch Pulverisette 5 (container volume 50 cm^3; ball/powder mass ratio=10:1) under rotation of 400 rpm for various time durations (15 mins to 1.5 hr) and the changes are monitored by PXRD patterns at regular intervals. Unlike Na_2CO_3 exceeding the milling time more than 1.5 hrs starts to oxidize Mn_3O_4 slowly and Mn_2O_3 began to appear. Bulk particles of Mn_3O_4 (Mn-HT) were synthesized by heating the commercial MnO at 1100°C for 12 hrs under ambient conditions. MnO nanoparticles were obtained by ball-milling the commercial MnO (99%, sigma) under rotation of 300 rpm for various time durations (15 mins to 1.5 hr). Exceeding the milling time more than 1.5 hrs start to oxidize it further as monitored by PXRD.

Characterizations: Phase identification was performed by PXRD analysis with a Bruker D8 Advance diffractometer using Cu Kα radiation. FESEM images and Energy Dispersive X-Ray analysis (EDAX) was carried out by FEI Nova Nanosem 600. Transmission electron microscope (TEM) images were recorded with FEI Technai T20 instrument at an accelerating voltage of 200 kV. BET measurements were performed in Quanta-chrome Autosorb instrument at 77K from N_2 absorption. Thermogravimetric analysis (TGA) was done using Perkin-Elmer Pyris1instrument. Dynamic light scattering measurements were carried out with Zetasizer Nano ZS (Malvern

Instruments). ICP measurements were carried out using a Perkin-Elmer Optima 7000 DV instrument. Oxide particles were digested in conc. HNO_3 (high pure, sigma-aldrich) and diluted with Millipore water for the measurements.

Reactivity Tests: Mn_3O_4 and Na_2CO_3 was mixed mechanically and placed in a Pt pan to hang inside the TG furnace. Mixture was heated upto 850°C (heating rate 20°C/min) under Ar (99.5%) and maintained for 1hr to investigate step 1. We have investigated the splitting of water by employing the experimental set up described in our earlier report.[1, 2] Manganese oxide (Mn_3O_4 or MnO) and Na_2CO_3 were mixed mechanically for 20 mins and packed to an alumina reaction tube supported in between thin layers of Al_2O_3. The reaction tube was placed inside the furnace and heated to reaction temperature (ramp rate 20°C/min) under continuous flow of N_2 (99.9999%, 50 cc/min). Water vapour was introduced in the reaction chamber by sweeping the N_2 through a water bubbler. The connection in between the furnace and water bubbler was insulated with heating tape to avoid water condensation. Evolved H_2 was detected and measured with a gas chromatograph (PerkinElmer Clarus ARNEL 580) equipped with a TCD detector while total amount of H_2 was calculated by the water displacement method. After H_2 evolution, Sodium was extracted by bubbling CO_2 (10 ml/min) through the aqueous dispersion of α-$NaMnO_2$ (0.5-2 wt%) at different temperature for different periods (Table S1). For O_2 desorption the hydrolyzed sample was heated upto 850°C (heating rate 5°C/min) under Ar.

Table S1. Physiochemical properties of Mn_3O_4 and Na_2CO_3 samples.

Samples	**Abbreviations**	**Crystal size (nm)**[b]	**Particle size**[c]	**Particle size Distribution in nm (avearge size)**[d]	**BET surface area (m^2/g)**	**% of CO_2 evolved within 600°C**[e]	**H_2 yield (%)**[f] **@850°C @80min**
Mn_3O_4-commercial	**Mn-C** [a]	43	1-2 µm	----------	~1	54.1	35
Mn_3O_4-high temp annealed	**Mn-HT** [a]	75	>3 µm	----------	<0.5	22.4	<15
Mn_3O_4-ball mill 30 min	**Mn-30** [a]	27	100-500 nm	70-1000 **(350)**	13	74.4	---------
Mn_3O_4-ball mill 60 min	**Mn-60** [a]	15	100-250 nm	70-1500 **(350)**	15	81	---------
Na_2CO_3-commercial	**Na-C**	48	~5 µm	----------	~1	---------	---------
Na_2CO_3-ball mill 30 min	**Na-30**	34	250nm-2 µm	----------	5	---------	---------
Na_2CO_3-ball mill 60 min	**Na-60**	30	250nm-1 µm	----------	6	---------	---------
Mn_3O_4& Na_2CO_3-ball mill 30 min	**MnNa-30**	---------	---------	----------	-------	96.4	69
Mn_3O_4& Na_2CO_3-ball mill 60 min	**MnNa-60**	---------	---------	---------	-------	97.54	75

[a] Samples are ground with commercial Na_2CO_3

[b] Calculated using Debey-Scherrer equation

[c] From FESEM analysis

[d] From DLS measurement

[e] $$\% \ of \ CO_2 \ evolved = \frac{experimentally \ measured \times 100}{theoretically \ calculated}$$

[f] measured over the H_2 collected at 850°C for 80 mins.

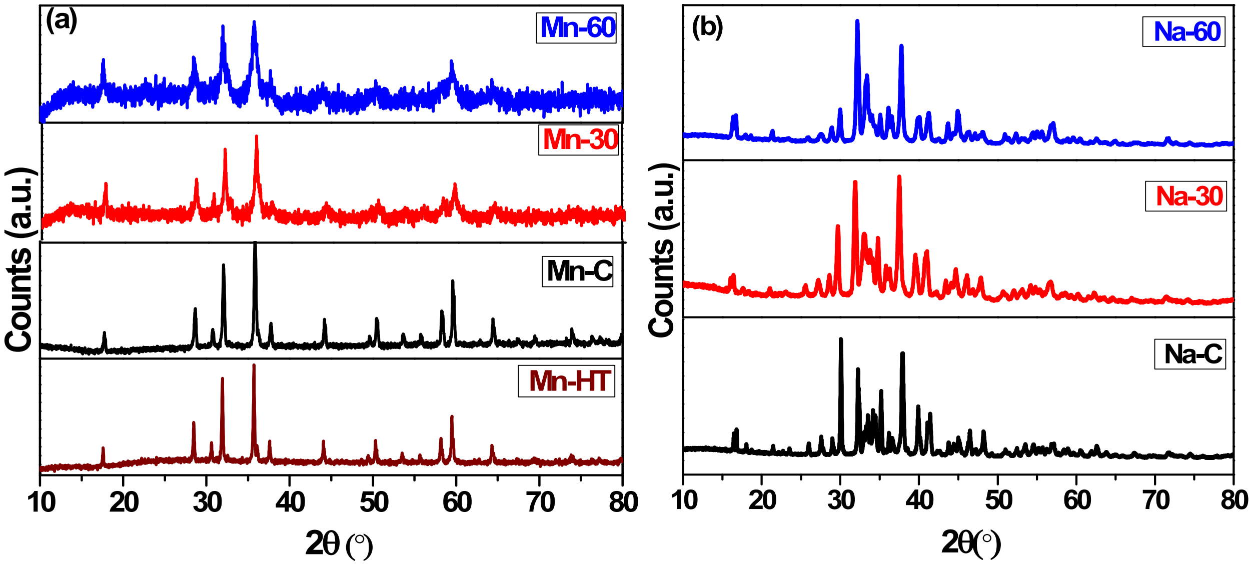

Figure S1. PXRD pattern of bulk and nanoparticles of (a) Mn_3O_4 and (b) Na_2CO_3.

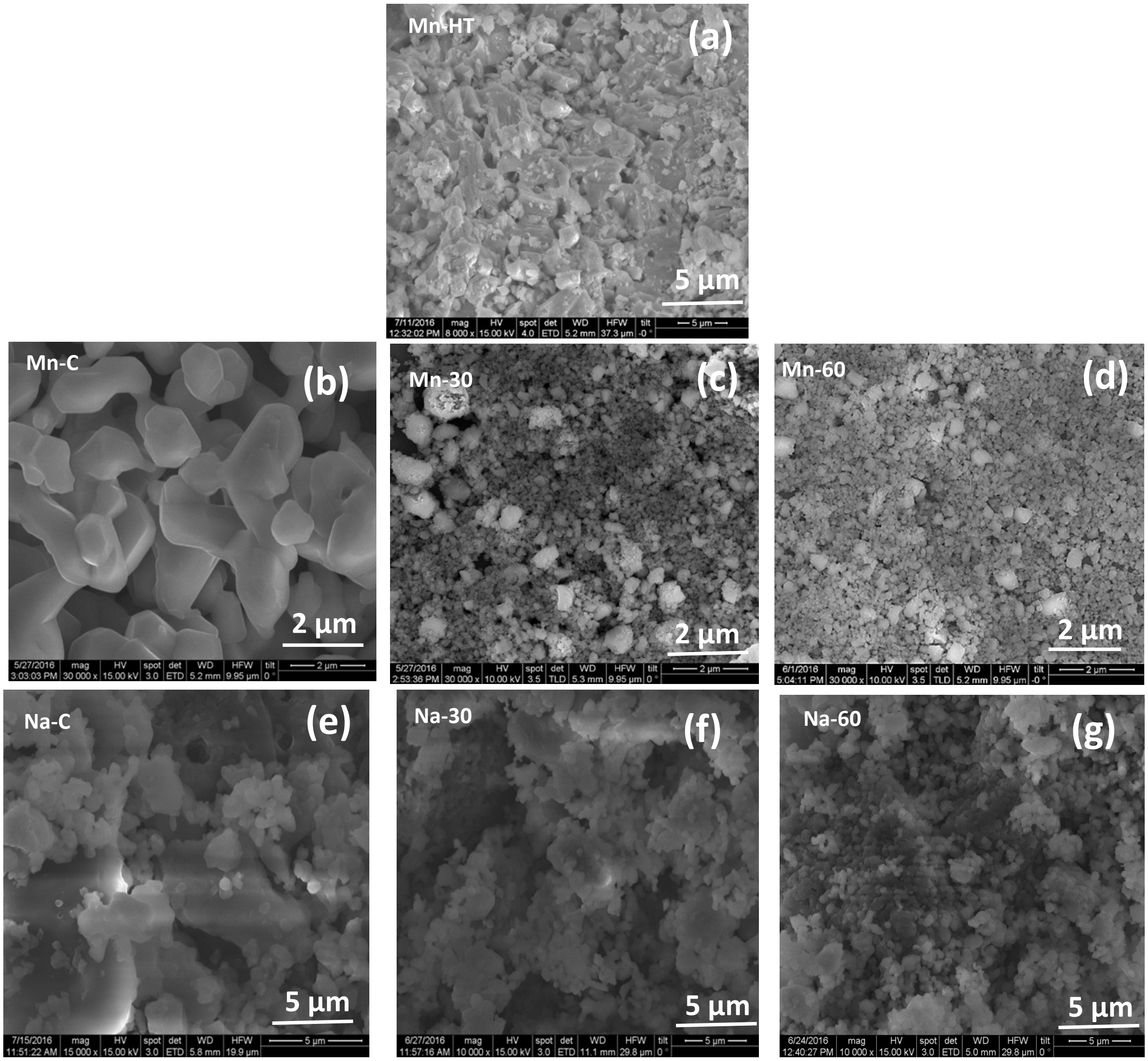

Figure S2. FESEM images of (a) high tempearture annealed Mn_3O_4 (Mn-HT), (b)commercial Mn_3O_4 (Mn-C),(c) 30 mins ball milled Mn_3O_4 (Mn-30), (d) 60 mins ball milled Mn_3O_4 (Mn-60), (e)commercial Na_2CO_3 (Na-C),(f) 30 mins ball milled Na_2CO_3 (Na-30) and (f) 60 mins ball milled Na_2CO_3 (Na-60).

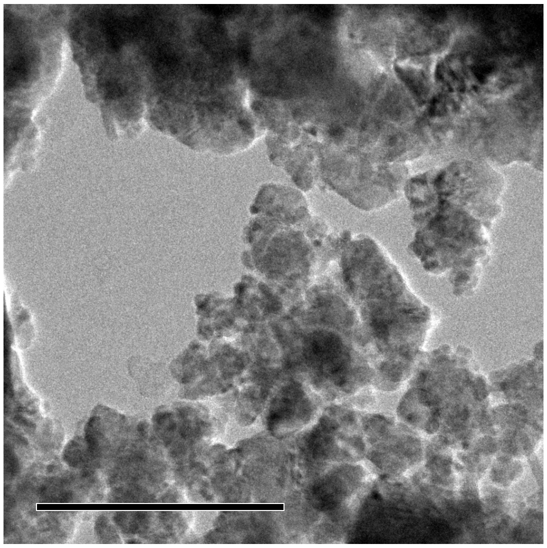

Figure S3. Transmission electron microscope (TEM) image of 60 mins ball milled Mn_3O_4 (Mn-60) shows the presence of nanoparticles (scale bar is of 200 nm).

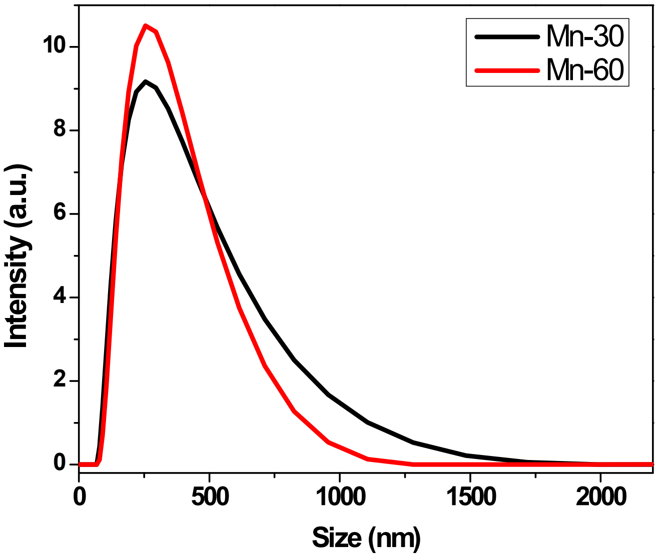

Figure S4. Dynamic light scattering measurements (DLS) show the particle size distributions of 60 mins and 30 mins ball milled Mn_3O_4 sample. Datas are also included in Table S1.

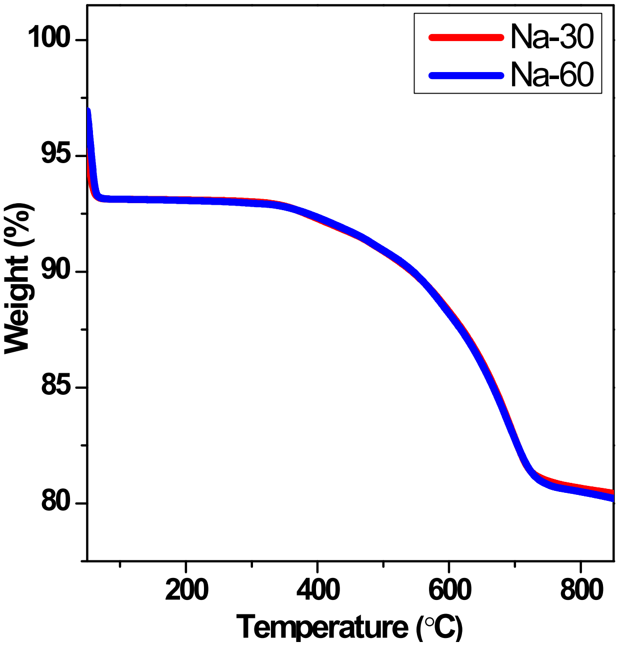

Figure S5. Thermogravimetric weight loss vs reaction temperature due to CO_2 evolution (step 1) for Mn_3O_4 (Mn-C) mixed with ball-milled Na_2CO_3. 30 and 60 represent the ball milling time in minutes.

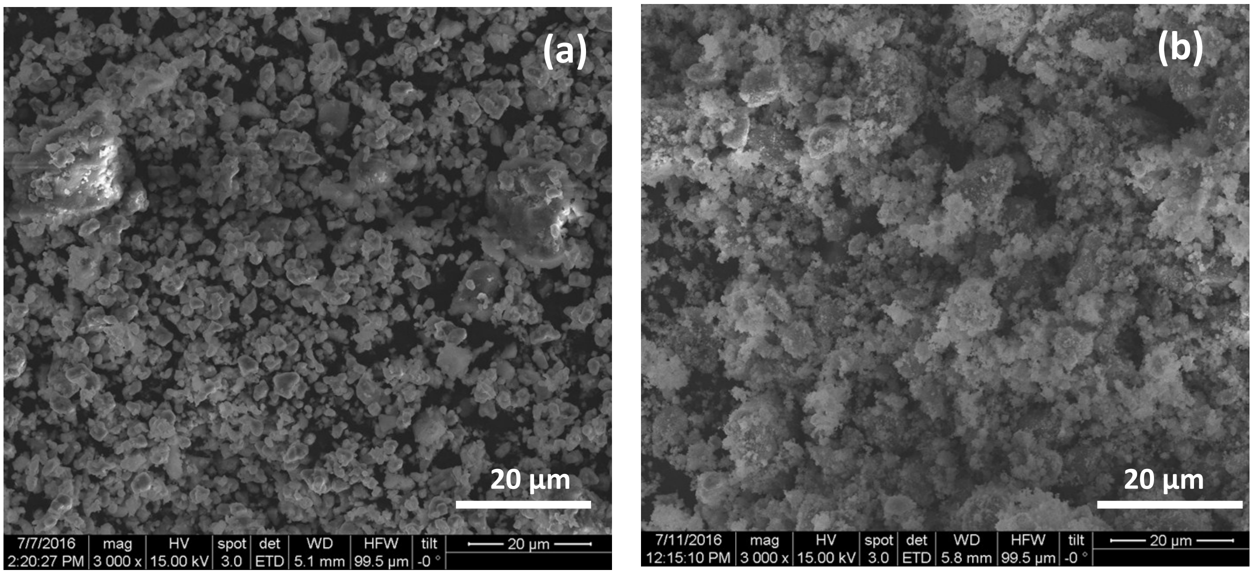

Figure S6. FESEM images of mixture of (a) commercial Mn_3O_4 with commercial Na_2CO_3 and (b) nanoparticles of both Mn_3O_4 and Na_2CO_3 (60 mins ball milled, MnNa-60). The mixture of commercial Na-C with Mn-C shows a phase separation while the nanoparticles result in more homogenous mixture due to their smaller particle sizes.

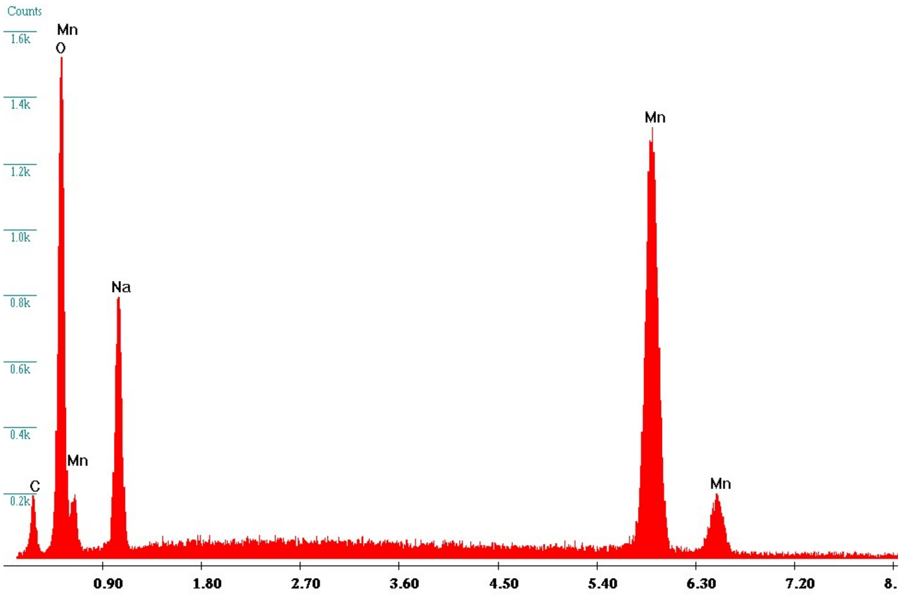

Figure S7. EDAX shows the uniform distribution Mn and Na throughout the nanoparticle samples of MnNa-60 (recorded at spot size of 500 nm). X and Y axis are Energy in KeV and counts respectively.

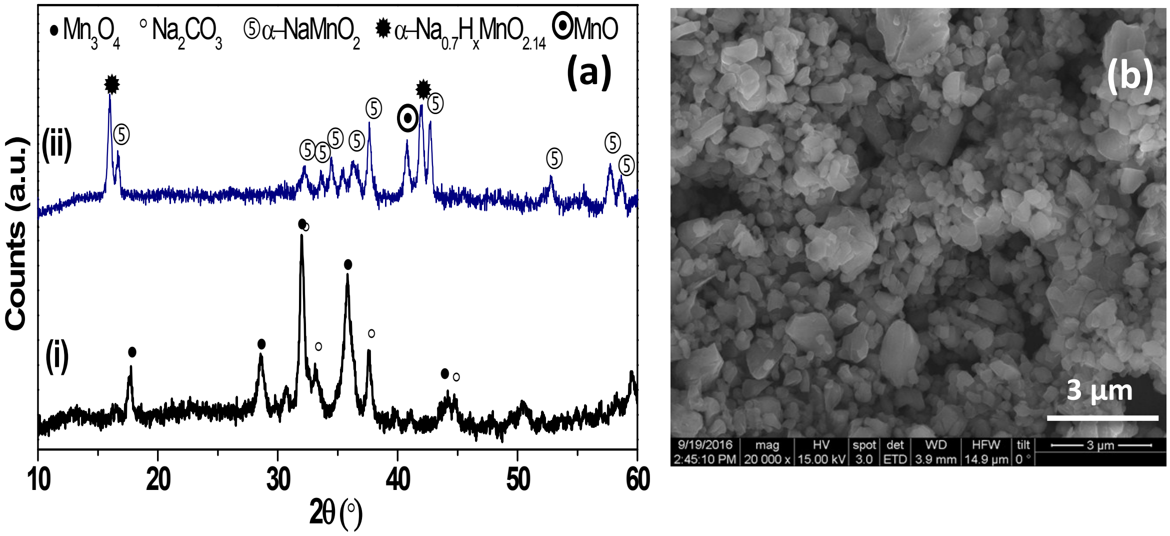

Figure S8. (a) Powder X-ray diffraction (PXRD) patterns of MnNa-60 before (i) and after (ii) step 1. Peaks shows the presence of (i) nanoparticles of Mn_3O_4+Na_2CO_3 and (ii) MnO, α-$NaMnO_2$ and α-$Na_{0.7}MnO_{2.14.}$

α-$Na_{0.7}MnO_{2.14}$ forms due to exposure of atmospheric moisture. (b) FESEM image to show the particles sizes of as formed products after step 1.

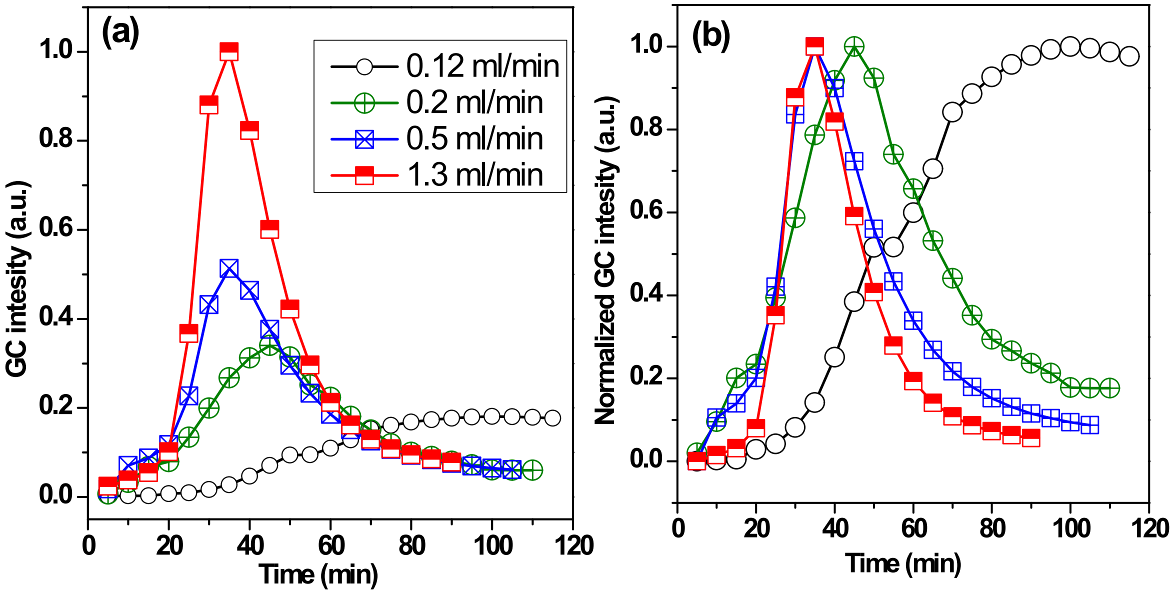

Figure S9. (a) Relative GC intesity to show the effect of H_2O flow rate on the production of H_2 during the oxidation of Mn_3O_4 to α-$NaMnO_2$ at 850°C (steps 1 and 2 together). Both Mn_3O_4 and Na_2CO_3 are commercial bulk sample. (b) GC intesity normalized with respect to peak position.

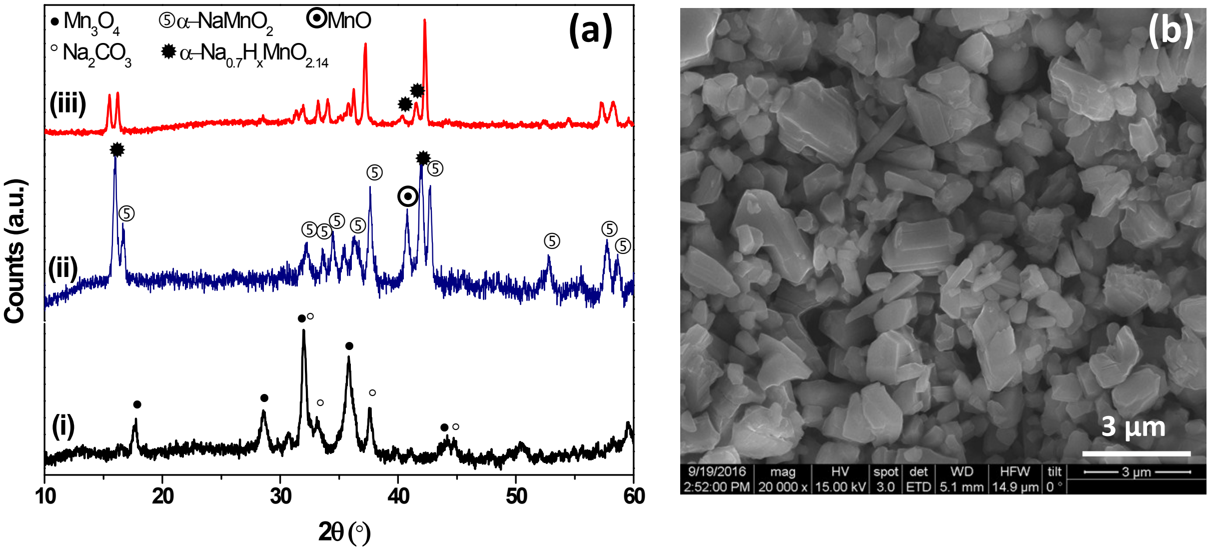

Figure S10. (a) PXRD patterns to identify the solid forms after H_2 evolution of MnNa-60 at 850°C (steps 1 and 2 together). (iii) After H_2 evolution α-$NaMnO_2$ and α-$Na_{0.7}MnO_{2.14}$ formed with the disappearance of MnO peaks. For comparison PXRD patterns of solids (i) before and (ii) after step

1 is given. (b) FESEM image to show the particles sizes of α-$NaMnO_2$ and α-$Na_{0.7}MnO_{2.14}$ formed after step 2.

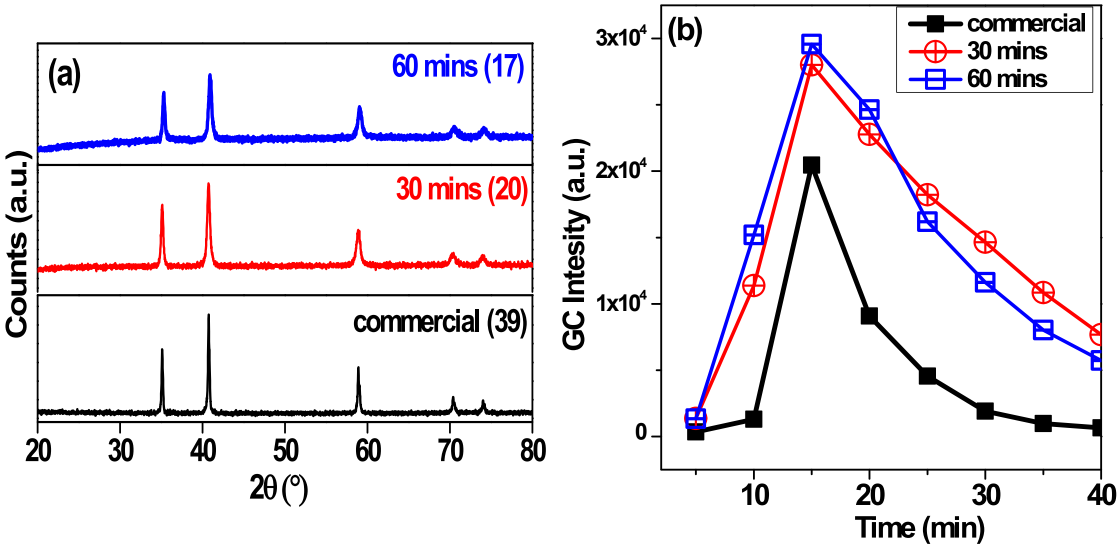

Figure S11. (a) PXRD reflections of bulk and nanoparticles (ball milled for 30 and 60 mins) of MnO. The crystal sizes are given in the parenthesis after each legend (unit is nm). (b) The H_2 evolution profile of reaction of MnO with Na_2CO_3 in presence of H_2O (step 2) at 850°C.

Serial no.	Weight % of sample [a, b]	Time (hr)	Temperature (°C)	PXRD [c]	~% Na recovery [d]
1 (Ref. conditions)	0.5	3	100	☑	97.5
2	0.5	3	**50**	☑	97
3	0.5	3	**25**	☒	-----
4	0.5	**1**	50	☑	97
5	0.5	**0.25**	50	☒	-----
6	**2**	1	50	☑	96.6

Table S2: Summary of CO_2 assisted hydrolysis step (Step 3).

[a] CO_2 buubling rate was 10 ml/min.

[b] Red mark is to specify the changes in condition during each step than reference conditions.

[c] '☑' indicates the detection of PXRD patterns after hydrolysis. '☒' indicates the formation of amorphous phase after hydrolysis.

[d] calculated from Na/Mn ratio obtained using EDAX and ICP analysis.

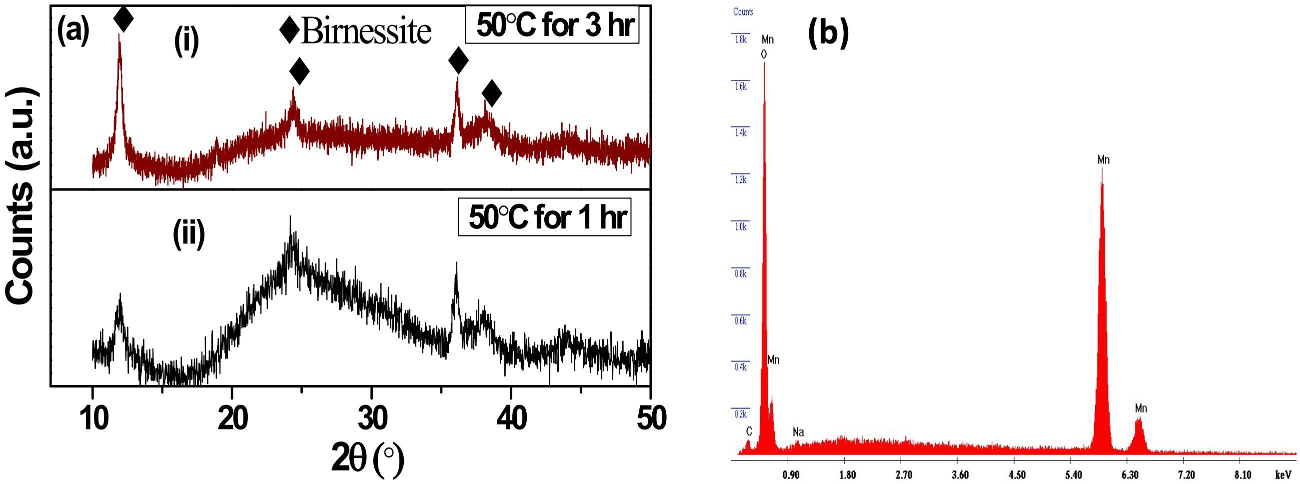

Figure S12. (a) PXRD patterns after CO_2 assisted hydrolysis of α-$NaMnO_2$ at 50°C for 3 hr (i) and 1 hr (ii) confirms the formation of protonic birnessite phase. (b) EDAX image of the product obtained after CO_2 assisted hydrolysis at 50°C for 1 hr. X and Y axis are Energy in KeV and counts respectively.

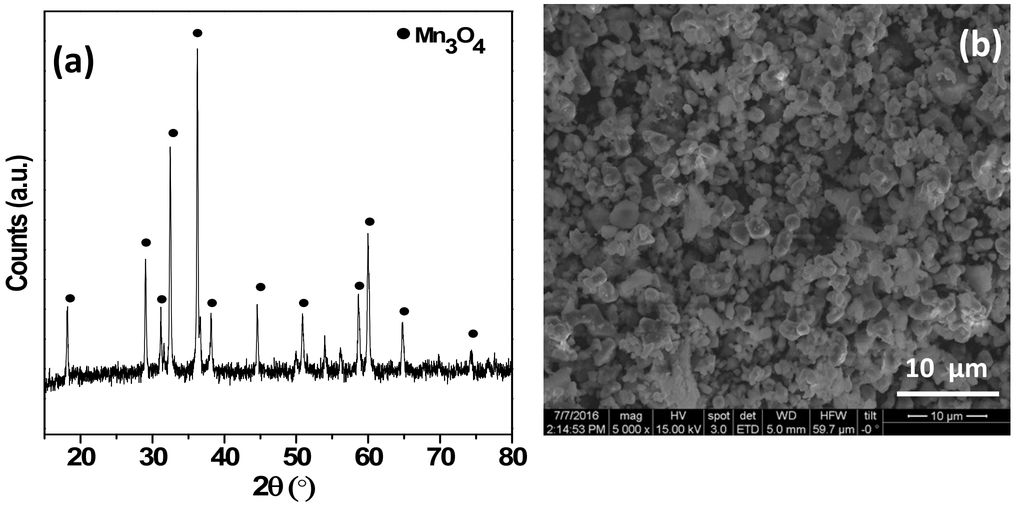

Figure S13. (a) PXRD of thermally reduced (~820°C, under Ar) Na^+ extracted α-$NaMnO_2$ confirms the formation of Mn_3O_4 in pure phase (Step 4). (b) FESEM image of this Mn_3O_4.

References:

1 S. Dey, B. S. Naidu, A. Govindaraj and C. N. R. Rao, *Phys. Chem. Chem. Phys.*, 2015, **17**, 122-125.
2 S. Dey, B. S. Naidu and C. N. R. Rao, *Chem. Eur. J.*, 2015, **21**, 7077-7081.