Electronic Supporting Information

Achieving Ambient Temperature Hydrogen Storage in Ultrafine Nanocrystalline TiO_2@C-doped $NaAlH_4$

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Table S1. Relative C and TiO_2 contents in the composite carbonised at 900 °C.

TiO_2@C	C (wt%)	TiO_2 (wt%)
TiO_2@C-900	31.20	68.79

Table S2. Comparison of hydrogen storage properties of catalysts-added $NaAlH_4$

References		[11]	[14]	[11,14]	[17]	[16]	[15]	[15, 21]	[20, 21,24]	[24]	[23]	[30]	[31]	**This work**
Hydrogen Storage properties		Catalysts												
		Nano-TiO_2	TiF_3	$TiCl_3$	Nano-TiN	TiB_2	$HfCl_4$	VCl_3	$ScCl_3$	$CeCl_3$	$CeAl_4$	TiO_2/C	TiO_2-OMCs	**TiO_2@C**
Dehydrogenation	On-set Temperature (°C)	120	--	100	125	70	85	135	150	--	--	100	60	**63**
	Terminal temperature (°C)	230	--	200	220	240	200	240	220	--	--	--	--	**170**
Isothermal dehydrogenation	Temperature (°C)	150	150	150	150	120	--	--	--	--	150	160	160	**140**
	Desorption Capacity (wt%)	4.5	4	□3.5	3.75	3	--	--	--	4.4	4.4	5.07	2.31	**4.5**
	Full Desorption time (min)	240	180	□600	25	400	--	--	--	50	35	100	□60	**30**
Dehydrogenation Capacity (wt%)		5.1	4	4.8	5.2	5.0	4.5	4.45	3.4	4.4	4.4	5.07	2.31	**4.5**
Re-hydrogenation Capacity (wt%)		4.6	3.7	4.3	4.7	3.0	2.9	2.0	3.1	4.4	4.4	4.72	2.15	**4.5**
Hydrogenation Pressure (bar)		--	110	110	--	40	--	--	100	105-94	102	100	100	**100**
Isothermal hydrogenation Temperature (°C)		--	100	100	--	100	--	--	125	120	120	120	120	**50 60 80**
Isothermal hydrogenation time (min)		--	360	600	--	540	--	--	15-20	35	25	60	960	**130 40 12**
Capacity Retention (%)/(cycles)		89.6 /(3)	95.5 /(10)	79.2/ (3)	82.7/(3)	57/(2)	54.4/(5)	33.7/(5)	85.3/ (10)	91/(30)	--	92/(10)	81/(10)	**98.9/(10)**

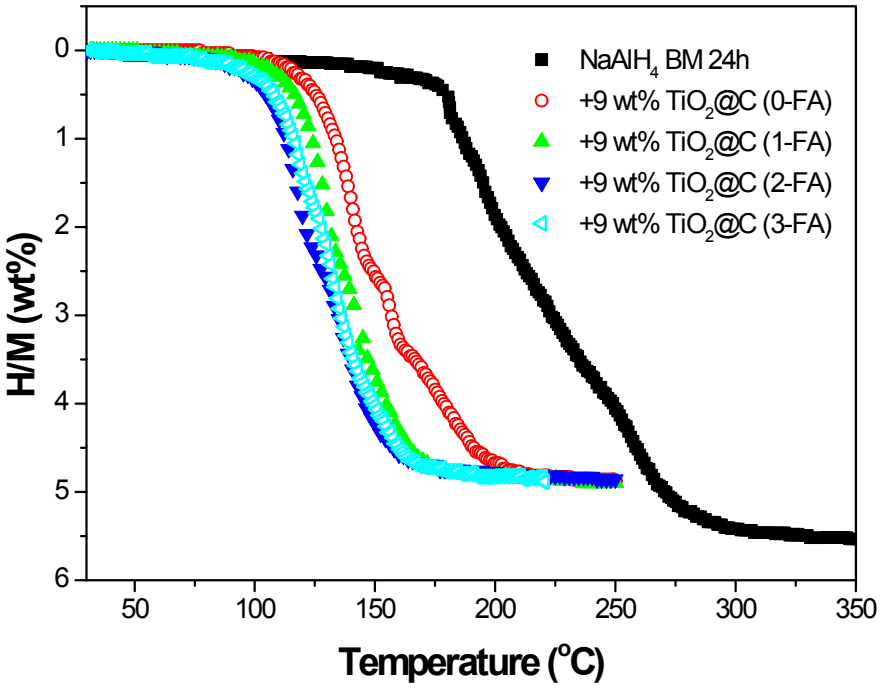

Figure S1 Comparison of the catalytic activities of the as-prepared TiO_2@C with different FA infiltration times (0: carbonised without FA, 1: infiltrated with FA only once, 2: infiltrated with FA twice, 3: infiltrated with FA three times).

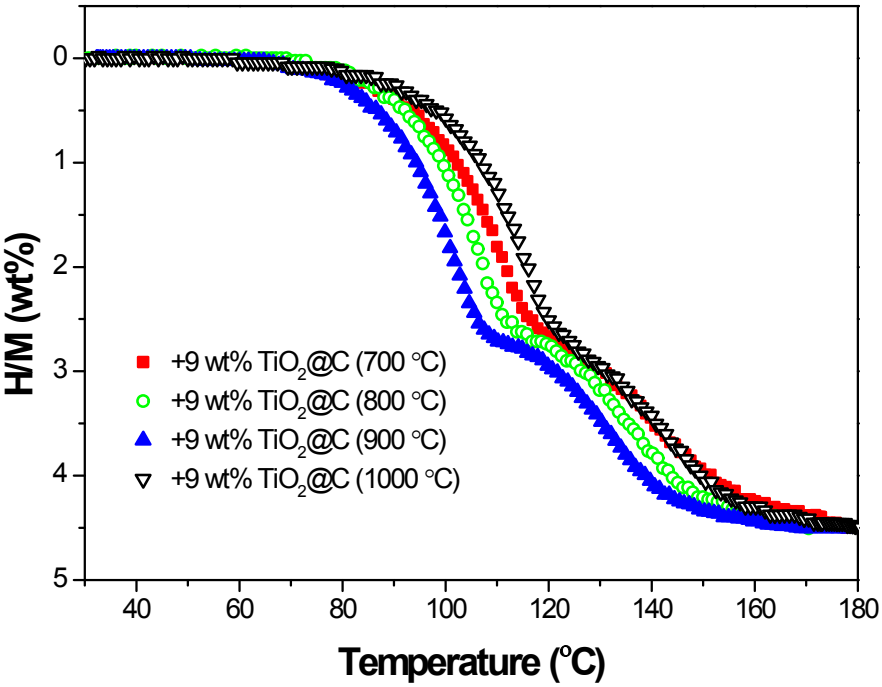

Figure S2 Comparison of the catalytic activities of the as-prepared TiO_2@C at different calcination temperatures.

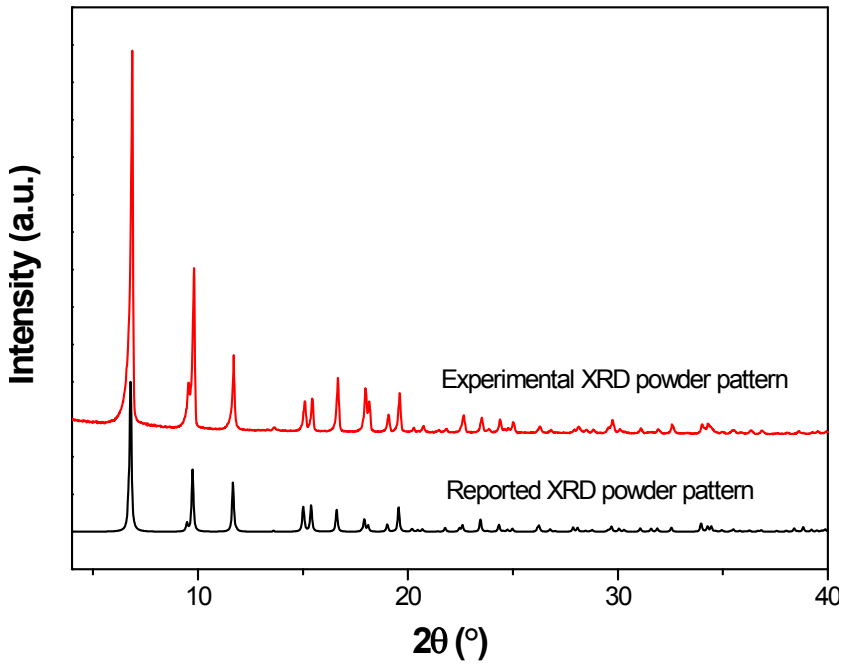

Figure S3 Experimental XRD pattern of the activated MIL-125(Ti) product compared with the reported XRD result.

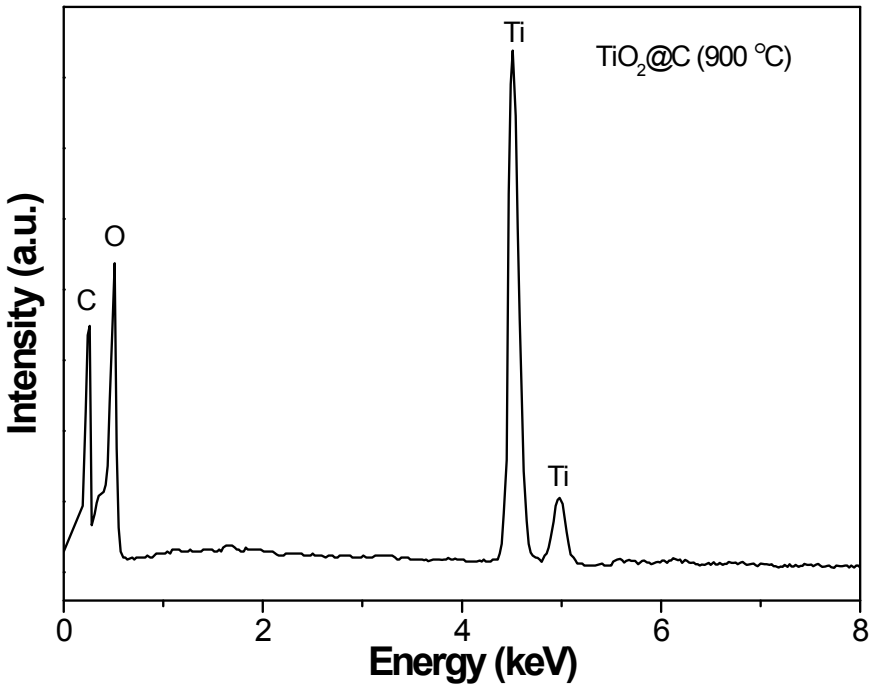

Figure S4 EDS result of the composite carbonised at 900 °C.

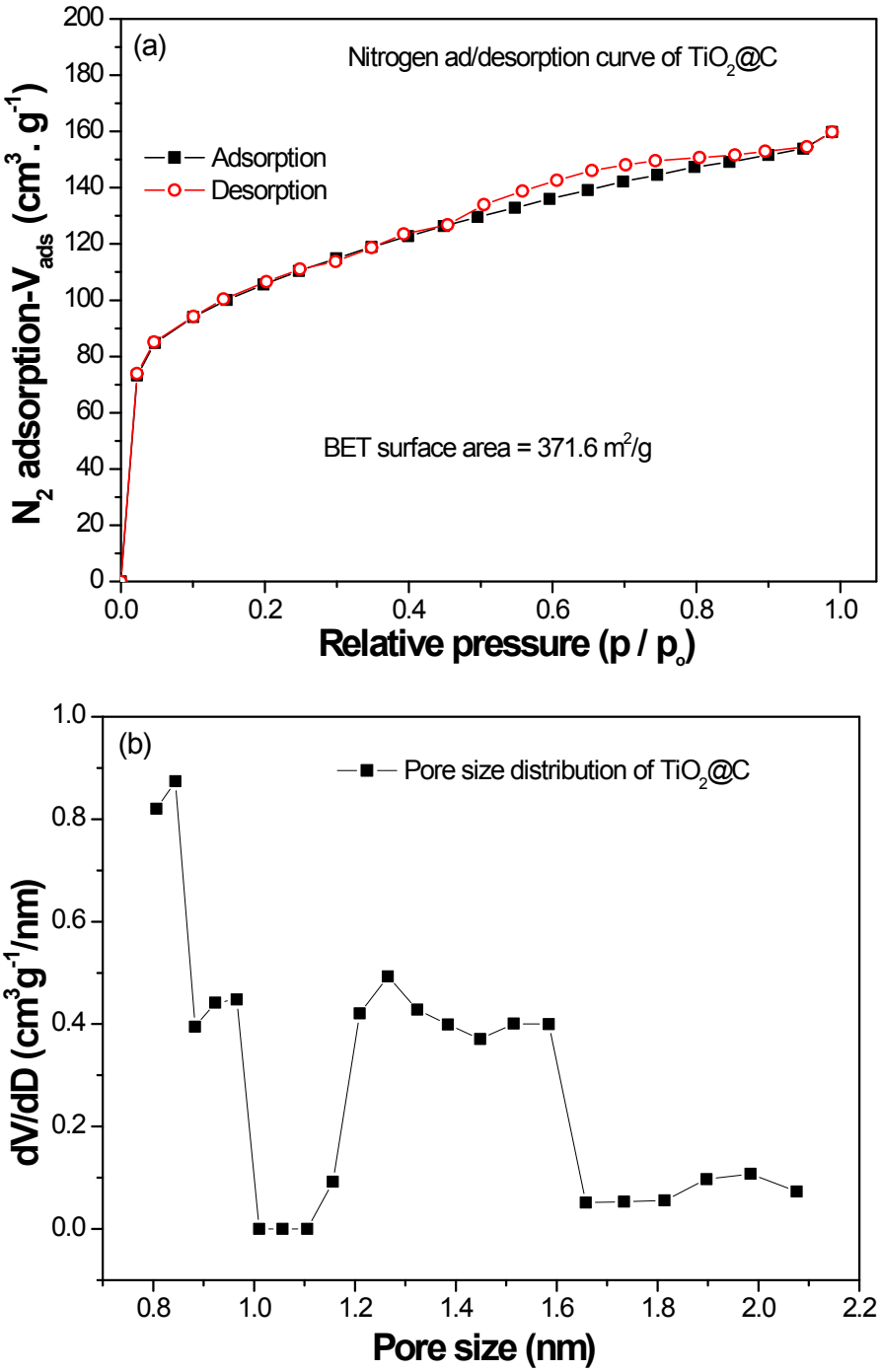

Figure S5 (a) N_2 adsorption/desorption isotherms and (b) pore size distribution of the as-prepared TiO_2@C sample at 900 °C.

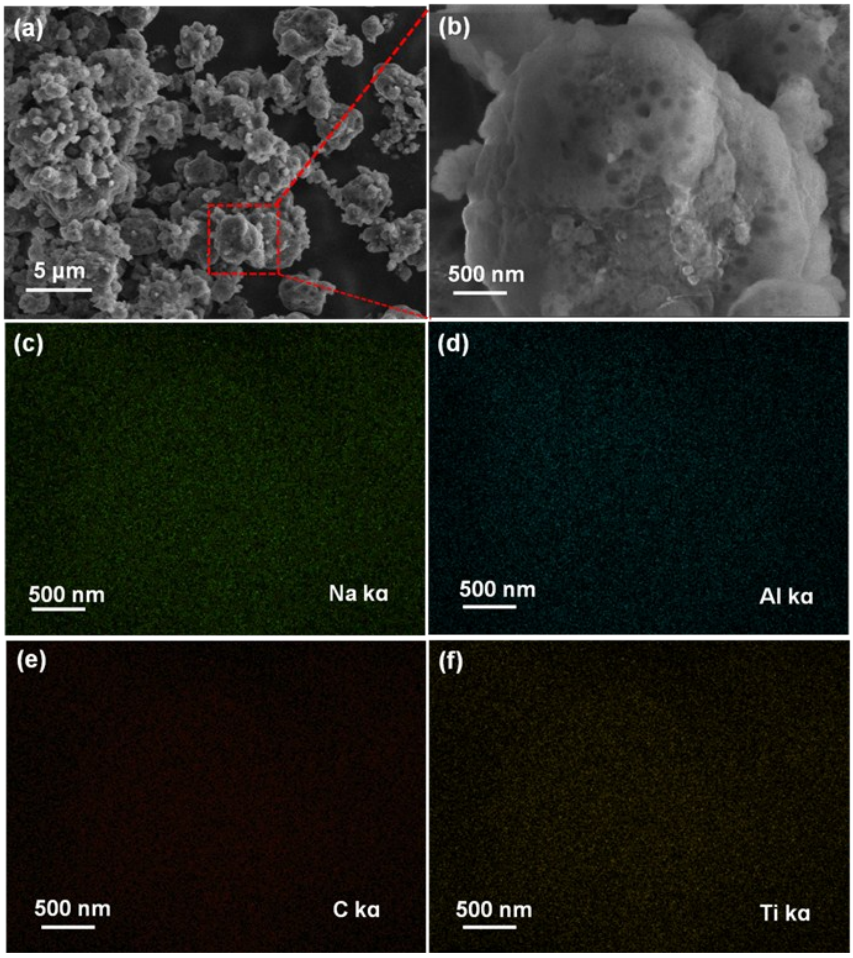

Figure S6 SEM images (a, b) and EDS maps of the elemental Na, Al, C, and Ti (c-f) in the TiO_2@C-added $NaAlH_4$ after ball milling.

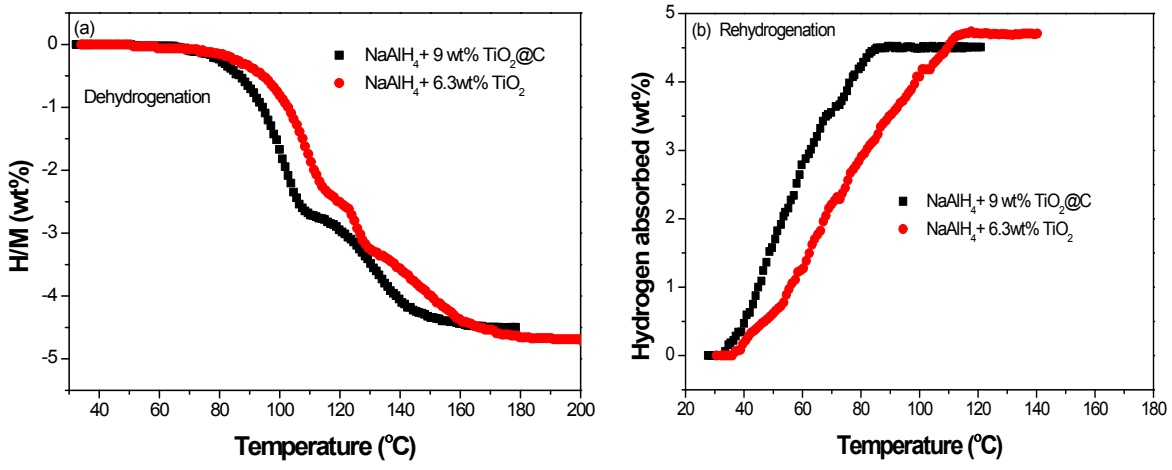

Figure S7 Non-isothermal dehydrogenation (a) and rehydrogenation (b) curves of the TiO_2@C- and pure TiO_2-added $NaAlH_4$ samples.

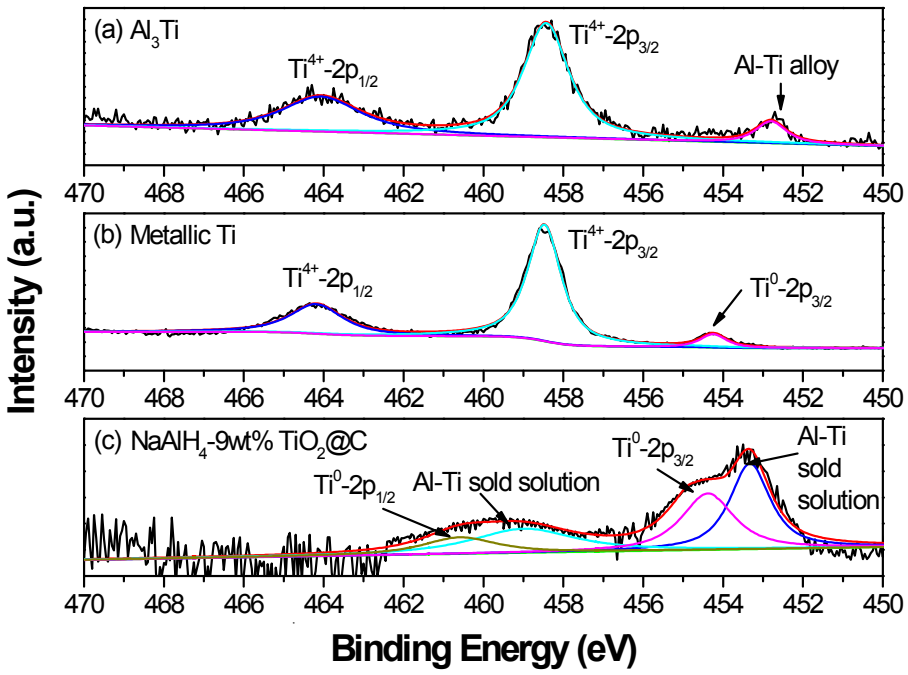

Figure S8 Ti 2p XPS spectra of the Al_3Ti (a), metallic Ti (Ti) and $NaAlH_4$-9 wt% TiO_2@C. (The presence of TiO_2 in the Al_3Ti and metallic Ti samples should be attributed to surface oxidation[S1])

Reference:

[S1] S. Seal, T. L. Barr, N. Sobczak, S. J. Kerber, *J. Mater. Sci.* 1998, **33**, 4147.

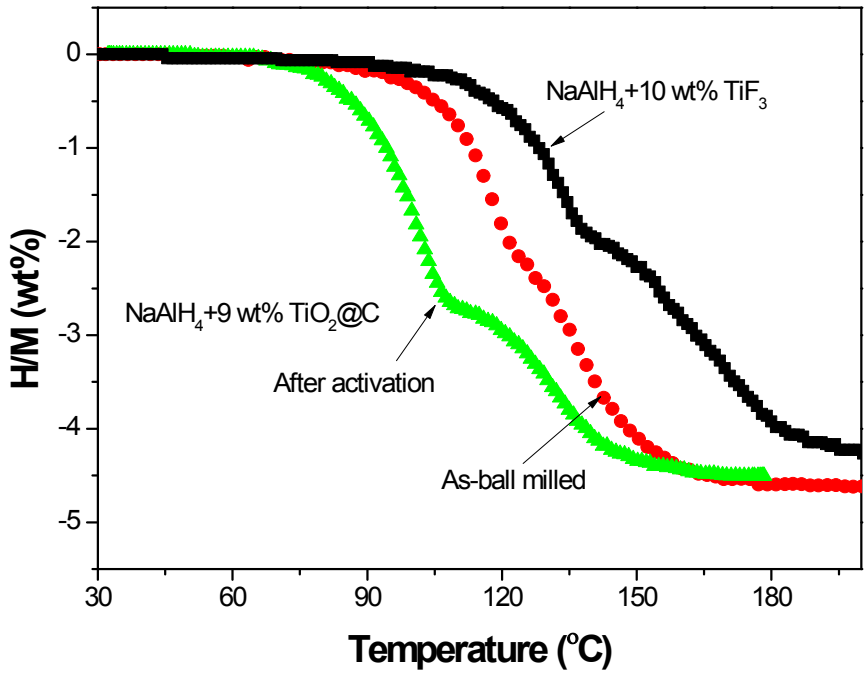

Figure S9 Non-isothermal dehydrogenation curves of TiO_2@C- and TiF_3-added $NaAlH_4$.

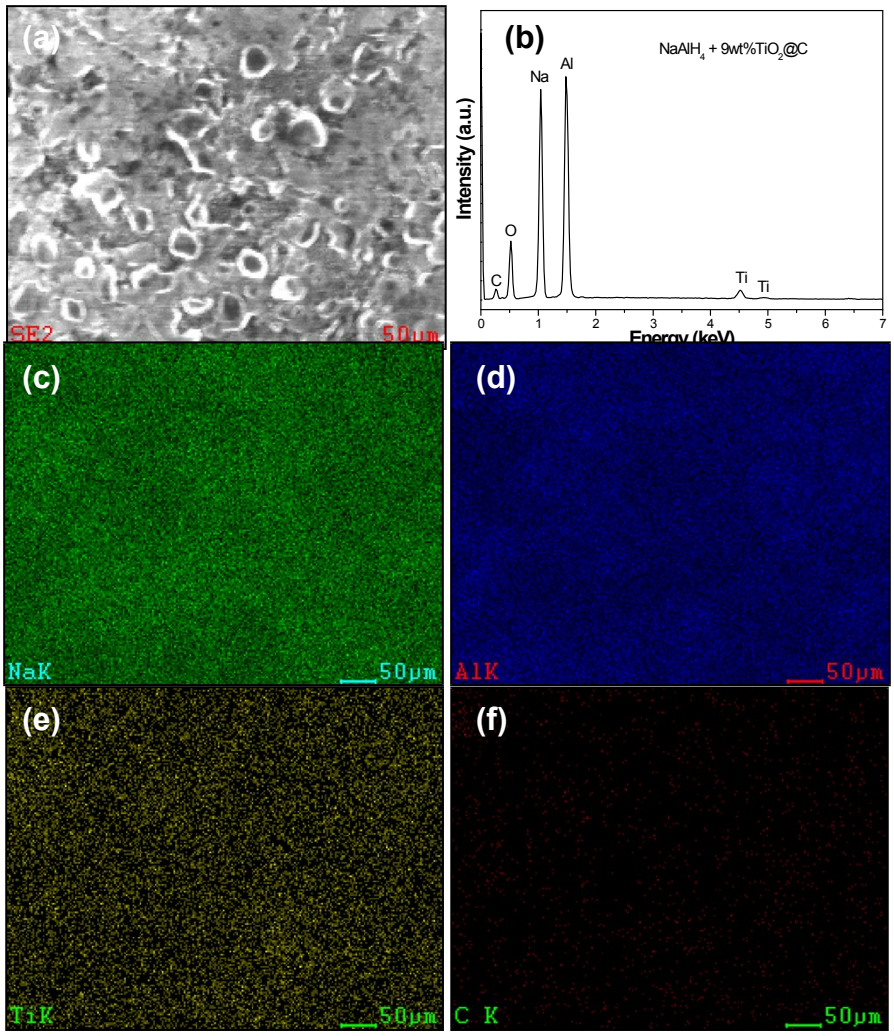

Figure S10 SEM image (a) and EDS spectrum and maps of the elemental Na, Al, Ti, and C (c-f) in the TiO_2@C-containing sample after 10 dehydrogenation/hydrogenation cycles.

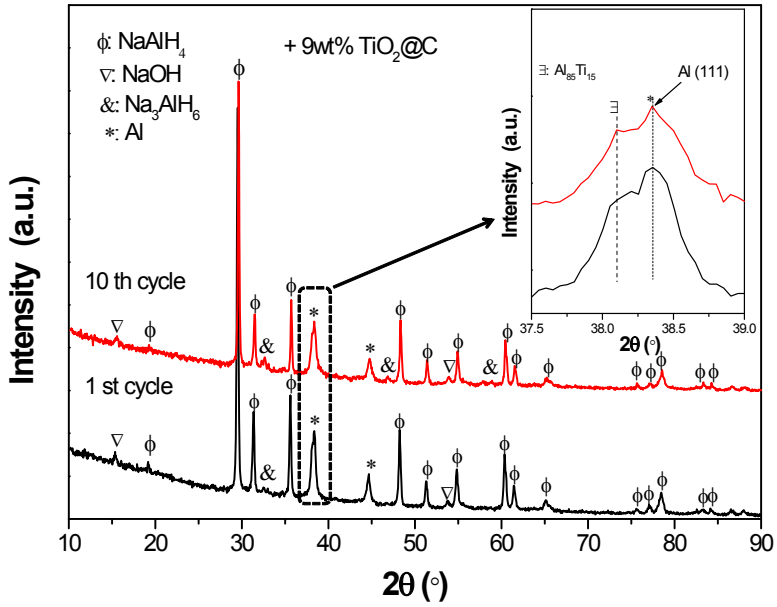

Figure S11 XRD patterns of the 9 wt% TiO_2@C-containing sample at different hydrogenation cycles.