SUPPLEMENTARY INFORMATION TO THE PAPER

AN OUTSTANDING EFFECT OF GRAPHITE IN NANO-MgH_2-TiH_2 ON HYDROGEN STORAGE PERFORMANCE

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Table S1. Summary of experimental conditions used during kinetic studies ("low-temperature" H absorption)

A. $Mg_{0.9}Ti_{0.1}$:

Cycle No.	Absorption				Desorption			
	***T*, °C**	***P*$_0$, bar**	***P*$_f$, bar**	**Δ*C*max, wt.%**	***T*, °C**	***P*$_0$, bar**	***P*$_f$, bar**	**Δ*C*max, wt.%**
0					330	0.001	0.23	6.3
1	100	10.25	5.5	5.19	330	0.19	0.40	5.58
2	100	10.2	5.9	4.74	330	0.2	0.39	5.29
3	100	10.3	6.2	4.5	330	0.2	0.39	5.04
4	330	10	8.9	5.82	330	1.05	2.14	5.95
5	100	10.3	6.65	4.01	330	0.22	0.38	4.78

B. $Mg_{0.9}Ti_{0.1}$ + 5% C:

Cycle No.	Absorption				Desorption			
	***T*, °C**	***P*$_0$, bar**	***P*$_f$, bar**	**Δ*C*max, wt.%**	***T*, °C**	***P*$_0$, bar**	***P*$_f$, bar**	**Δ*C*max, wt.%**
0					330	0.001	0.235	5.96
1	100	10.3	4.7	5.58	330	0.19	0.42	5.78
2	100	10.4	4.8	5.6	330	0.19	0.42	5.77
3	100	10.5	4.7	5.68	330	0.19	0.42	5.78
4	330	10	8.7	6.01	330	1.0	2.2	5.97
5	100	10.5	4.8	5.67	330	0.19	0.42	5.78
6	150	10.5	4.7	5.74	330	0.19	0.42	5.79
7	100	10.4	4.8	5.64	330	0.19	0.42	5.78
8	24	10.3	5.5	4.85	330	0.18	0.41	5.79
9	200	10.4	4.5	5.89	330	0.19	0.42	5.80
10	100	10.5	4.8	5.62	330	0.2	0.42	5.77
11	125	10.4	4.7	5.75	330	0.19	0.42	5.77
12	75	10.3	5.1	5.23	330	0.19	0.42	5.75
13	125	10.4	4.7	5.65	330	0.19	0.42	5.80
14	150	10.4	4.8	5.60	330	0.2	0.42	5.78
15	100	10.35	6.67	5.65	330	1	2.20	5.94[1]
16	200	10.25	4.45	5.93	330	0.18	0.40	5.79

(to be continued)

[1] After holding the sample at the H_2 pressure and room temperature for 1 week

Table S1 (B) – continued

Cycle No.	Absorption				Desorption			
	***T*, °C**	**P_0, bar**	**P_f, bar**	**ΔCmax , wt.%**	***T*, °C**	**P_0, bar**	**P_f, bar**	**ΔCmax , wt.%**
17	50	10.24	5.32	4.96	330	0.2	0.41	5.77
18	135	10.5	4.69	5.76	330	0.2	0.44	5.84
19	170	10.5	4.68	5.80	330	0.19	0.41	5.77
20	100	10.33	4.495	5.79	330	0.19	0.41	5.73
21	120	10.53	4.797	5.69	330	0.2	0.427	5.74
22	80	10.37	5.152	5.23	330	0.19	0.417	5.73
23	140	10.36	4.563	5.75	330	0.188	0.413	5.74
24	160	10.5	4.647	5.84	330	0.189	0.415	5.74
25	100	10.34	4.948	5.35	330	0.2	0.415	5.71
26	180	10.48	4.684	5.81	330	0.181	0.407	5.77
27	330	9.9	8.6	6.01	330	1.04	2.21	5.94
28	220	10.5	4.62	5.93	330	0.192	0.416	5.76
29	200	10.5	4.48	5.92	330	0.189	0.414	5.75
30	100	10.42	4.9	5.47	330	0.065	0.29	5.75
31	350	10.3	9.1	6.01	350	0.12	0.35	5.83
32	320	10.3	9.1	6.01	320	0.12	0.35	5.84
33	300	10.2	9.0	6.0	300	0.12	0.35	5.83
34	280	10.2	9.0	5.97	280	0.12	0.35	5.83
35	100	10.41	4.725	5.64	330	0.181	0.401	5.69
36	100	10.38	4.88	5.51	330	0.188	0.41	5.66
37	330	9.9	8.7	5.97	330	1.04	2.22	5.97
38	330	10.1	8.85	6.01	330	1.04	2.22	5.98
39	200	10.6	4.6	5.92	330	0.188	0.413	5.75
40	100	10.39	4.865	5.49	330	0.185	0.406	5.65
41	330	10	8.8	6.02	330	1.06	2.24	5.97
42	330	10	8.8	5.98	330	1.04	2.21	5.96
43	330	10.1	8.9	5.97	330	1.04	2.22	5.96
44	330	10	8.8	5.99	330	1.04	2.22	5.95
45	100	10.5	4.84	5.62	330	0.189	0.412	5.65
46	330	9.9	8.68	6.02	330	1.04	2.22	5.94
47	330	10	8.8	5.99	330	1.04	2.22	5.95
48	330	10	8.8	5.97	330	1.04	2.22	5.97
49	200	10.5	4.56	5.93	330	0.191	0.416	5.73
50	100	10.33	4.65	5.63	Unloaded in the hydrogenated state			

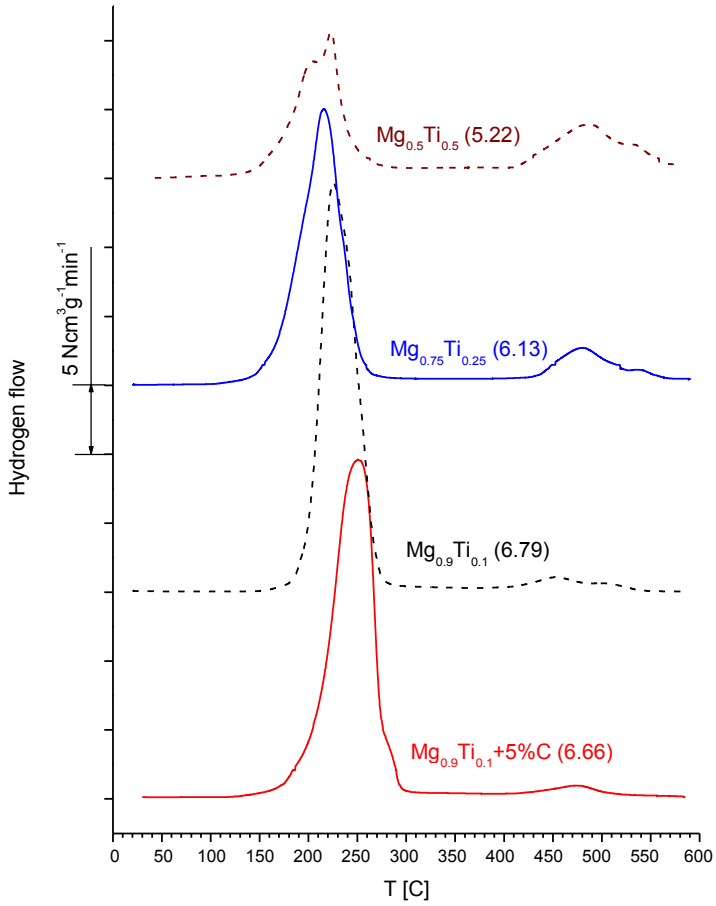

Figure S1.

TDS curves for the as-prepared materials. The values in brackets next to the curve labels specify the total amounts of hydrogen [wt.%] desorbed from the samples.

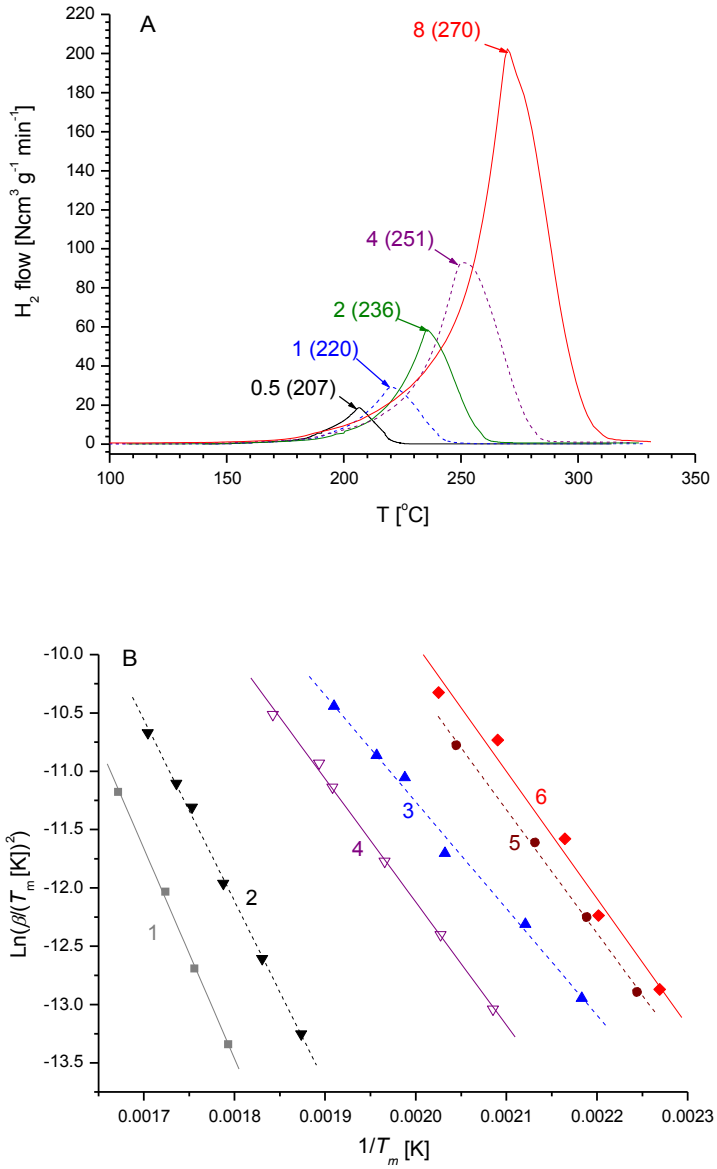

Figure S2.

A – TDS curves for $Mg_{0.9}Ti_{0.1}$+5% C; curve labels correspond to the heating rates [°C min^{-1}] followed by the peak temperature [°C] in brackets.

B – Kissinger plots for Mg (1), Mg + 5% C (2), $Mg_{0.9}Ti_{0.1}$ (3), $Mg_{0.9}Ti_{0.1}$ + 5% C (4), $Mg_{0.75}Ti_{0.25}$ (5), and $Mg_{0.5}Ti_{0.5}$ (6).

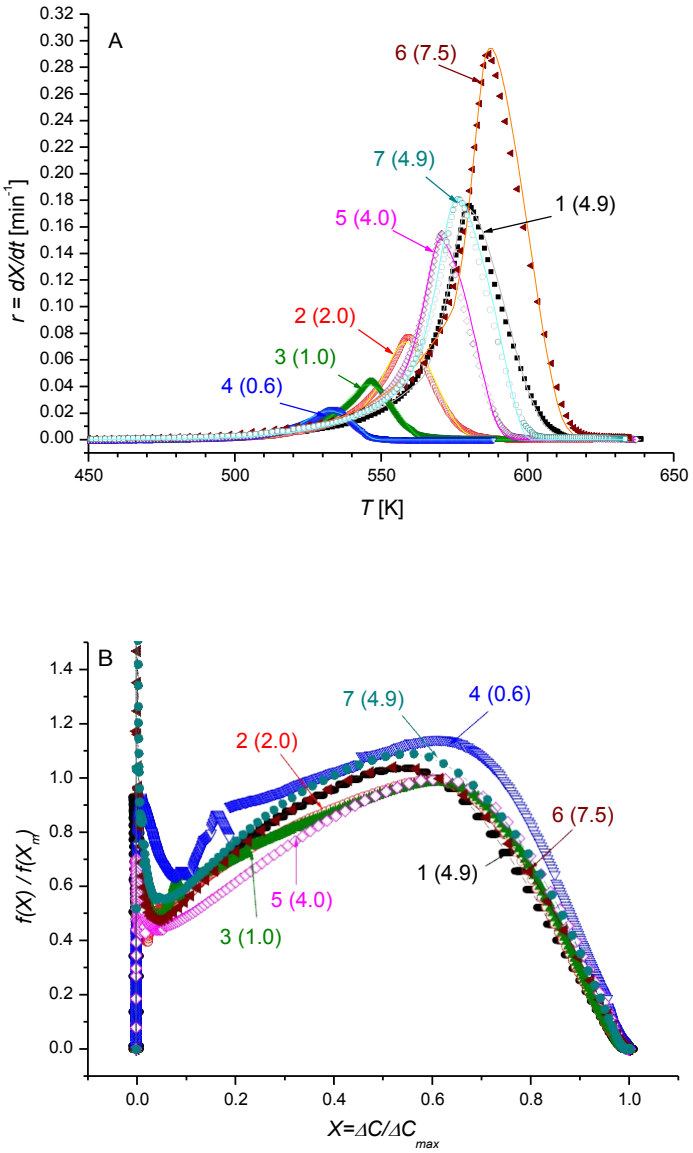

Figure S3.

Experimental (points) and calculated (lines) thermal desorption spectra (A) and rate dependence functions (B) derived from the experimental TDS data for Mg + 5% C.

Curve captions correspond to cycle number followed by the average heating rate [K min^{-1}] (in brackets).

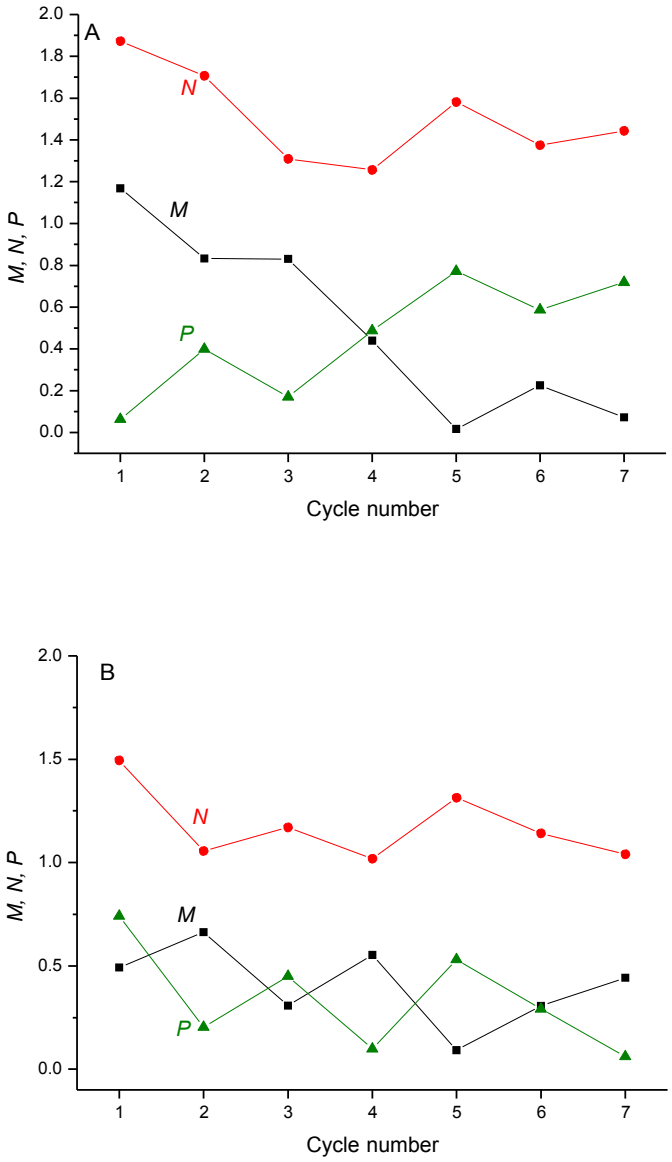

Figure S4.

Dependence of fitting parameters (Eq. 4 in the main text) on the number of re-hydrogenation – dehydrogenation cycle for $Mg_{0.9}Ti_{0.1}$ (A) and $Mg_{0.9}Ti_{0.1}$ + 5% C (B).

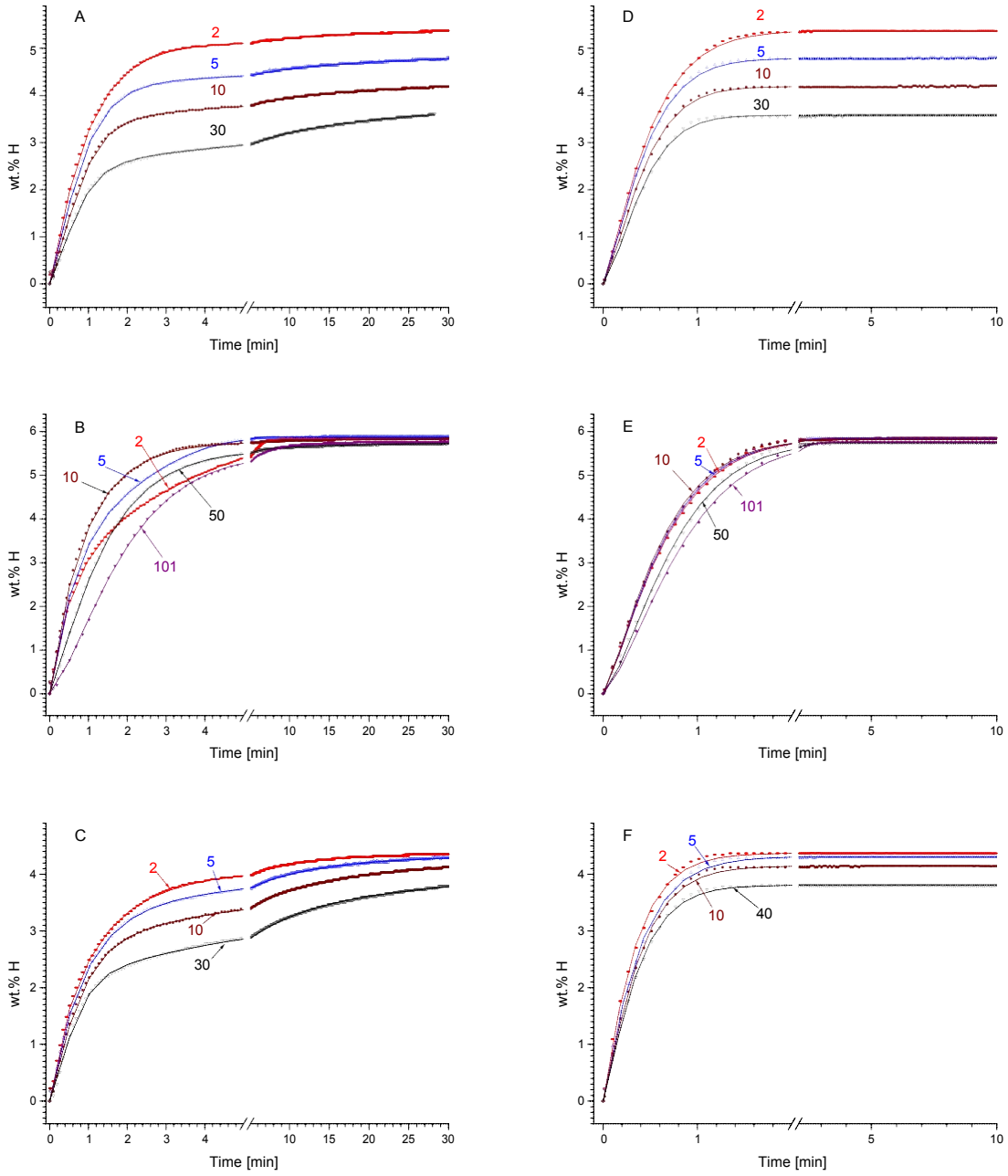

Figure S5.

Hydrogen absorption (A–C) and desorption (D–F) kinetics at T=350 °C (experimental points and calculated curves) for the samples $Mg_{0.9}Ti_{0.1}$ (A, D), $Mg_{0.9}Ti_{0.1}$ + 5% C (B, E) and $Mg_{0.75}Ti_{0.25}$ (C, F). Curve labels correspond to the numbers of the absorption/desorption cycle.

Table S2. Parameters of H absorption kinetics during cycling (T=350°C).

Sample	Cycle number (wt.% H observed)	Fitting parameters (Eq. 6)[2]								
		A_1 [wt% H]	k_1 [min^{-1}]	n_1	A_2 [wt% H]	k_2 [min^{-1}]	n_2	$N_{max}=A_1+A_2$ [wt% H]	$w_2=A_2/N_{max}$	R^2
$Mg_{0.9}Ti_{0.1}$	2 (5.38)	4.94(8)	1.032(4)	1.092(8)	0.5(1)	0.072(6)	0.8(2)	5.44	0.09	0.9995
	5 (4.80)	3.91(6)	1.132(7)	1.28(2)	1.01(8)	0.105(9)	0.57(5)	4.92	0.21	0.9993
	10 (4.19)	3.05(5)	1.163(8)	1.41(2)	1.24(6)	0.15(1)	0.57(3)	4.29	0.29	0.9992
	30 (3.61)	2.11(6)	1.25(1)	1.47(4)	1.77(1.9)	0.096(4)	0.61(3)	3.88	0.46	0.9990
$Mg_{0.9}Ti_{0.1}$ + 5%C	2 (5.85)	4.07(8)	1.35(5)	0.93(1)	1.77(8)	0.234(4)	2.13(6)	5.84	0.30	0.9997
	5 (5.88)	4.2(1)	1.45(6)	1.04(1)	1.6(1)	0.330(9)	2.2(1)	5.80	0.28	0.9997
	10 (5.83)	5.78(2)	1.066(5)	0.962(4)	0.2(1)	0.01(9)	1.3(5)	5.98	0.03	0.9994
	50 (5.73)	5.5(1)	0.678(5)	1.175(8)	0.3(1)	0.10(3)	1.0(4)	5.80	0.05	0.9996
	101 (5.78)	5.2(2)	0.50(1)	1.37(1)	0.6(2)	0.12(3)	1.6(4)	5.80	0.10	0.9997
$Mg_{0.75}Ti_{0.25}$	2 (4.36)	3.80(7)	1.00(2)	0.901(6)	0.58(8)	0.10(1)	1.0(1)	4.38	0.13	0.9995
	5 (4.29)	3.16(9)	1.13(1)	1.00(1)	1.2(1)	0.13(1)	0.83(7)	4.36	0.28	0.9995
	10 (4.13)	2.24(8)	1.24(1)	1.23(3)	2.02(9)	0.148(7)	0.64(3)	4.26	0.47	0.9994
	40 (3.79)	1.64(6)	1.41(1)	1.49(5)	2.39(7)	0.118(3)	0.64(2)	4.03	0.59	0.9993

Table S3. Parameters of H desorption kinetics during cycling (T=350°C).

Sample	Cycle number (wt.% H observed)	Fitting parameters (Eq. 5)			
		N_{max} [wt% H]	k [min^{-1}]	n	R^2
$Mg_{0.9}Ti_{0.1}$	2 (5.37)	5.374(2)	1.899(5)	1.230(6)	0.9996
	5 (4.80)	4.790(2)	2.064(8)	1.29(1)	0.9992
	10 (4.21)	4.188(2)	2.111(9)	1.36(1)	0.9992
	30 (3.58)	3.580(3)	2.14(1)	1.43(2)	0.9984
$Mg_{0.9}Ti_{0.1}$ + 5%C	2 (5.85)	5.855(4)	1.419(6)	1.26(1)	0.9991
	5 (5.84)	5.852(4)	1.455(6)	1.261(9)	0.9992
	10 (5.83)	5.835(5)	1.506(5)	1.262(8)	0.9993
	50 (5.74)	5.752(5)	1.236(6)	1.39(1)	0.9987
	101 (5.76)	5.767(5)	1.104(5)	1.40(1)	0.9995
$Mg_{0.75}Ti_{0.25}$	2 (4.37)	4.375(2)	2.86(2)	1.09(1)	0.9987
	5 (4.31)	4.310(2)	2.53(1)	1.10(1)	0.9987
	10 (4.14)	4.145(2)	2.50(1)	1.16(1)	0.9989
	40 (3.80)	3.807(2)	2.57(1)	1.19(1)	0.9989

[2] Here and below the references relate to the main text of the paper

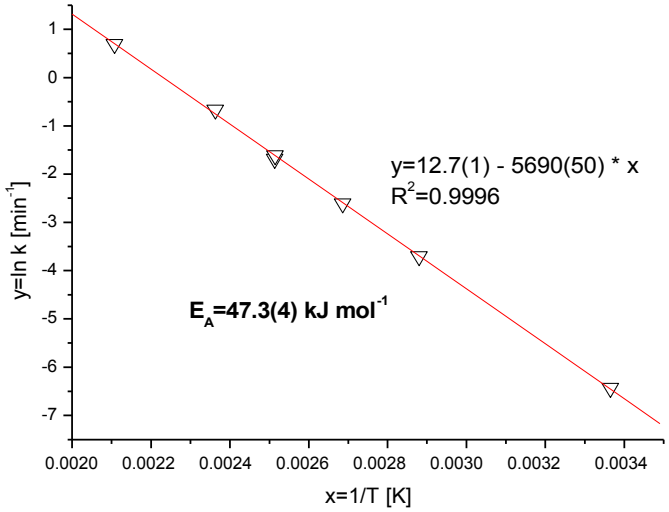

Figure S6.

Arrhenius plot of the rate constant for hydrogen absorption in $Mg_{0.9}Ti_{0.1}$ + 5% C calculated by the fitting of the experimental data (Figure 4A) with Eq. 5.

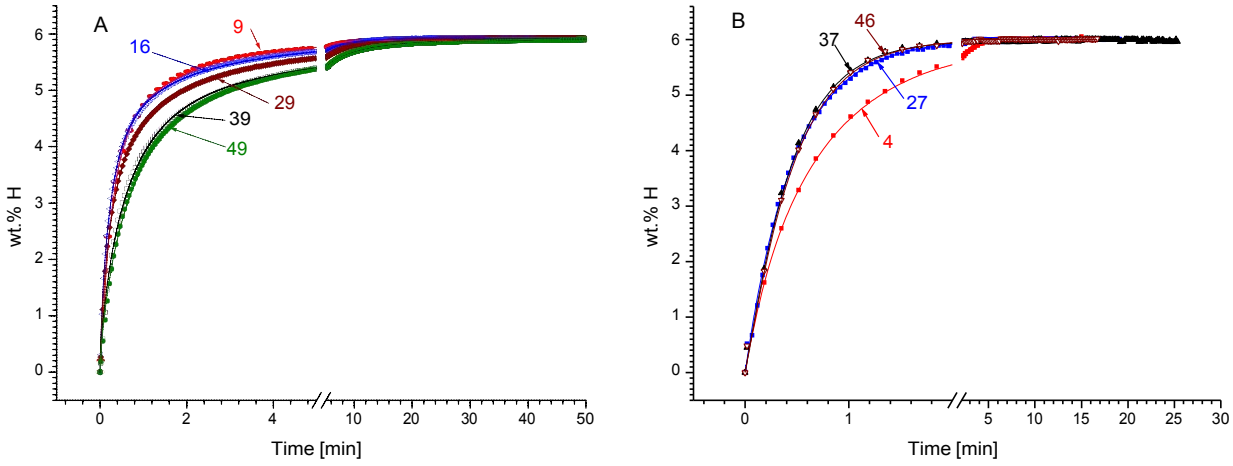

Figure S7.

Hydrogen absorption kinetics for the sample $Mg_{0.9}Ti_{0.1}$ + 5% C. A – at T=200°C; B – at T=330 °C.

Curve labels correspond to the number of the absorption/desorption cycle.

TableS4. Parameters of H absorption kinetics during cycling (T=100 °C).

Sample	Cycle number (wt.% H observed)	Fitting parameters (Eq. 6)								
		A_1 [wt% H]	k_1 [min^{-1}]	n_1	A_2 [wt% H]	k_2 [min^{-1}]	n_2	$N_{max}=A_1+A_2$ [wt% H]	$w_2=A_2/N_{max}$	R^2
$Mg_{0.9}Ti_{0.1}$	1 (5.19)	4.03(3)	0.481(4)	0.500(2)	1.35(4)	0.0041(1)	0.47(2)	5.38	0.25	0.9982
	2 (4.74)	3.21(5)	0.481(3)	0.500(4)	1.93(7)	0.00274(5)	0.40(2)	5.14	0.38	0.9974
	3 (4.50)	3.37(5)	0.318(2)	0.500(4)	1.8(2)	0.0007(1)	0.40(3)	5.17	0.35	0.9964
	5 (4.01)	2.48(3)	0.2839(8)	0.500(2)	2.02(5)	0.00182(2)	0.400(9)	4.50	0.45	0.9997
$Mg_{0.9}Ti_{0.1}$ + 5%C	1 (5.61)	4.22(4)	0.0396(1)	0.820(2)	1.44(5)	0.0055(2)	0.74(2)	5.66	0.25	0.9999
	2 (5.63)	4.18(7)	0.03551(5)	0.822(3)	1.45(7)	0.0086(5)	0.71(2)	5.63	0.26	0.9999
	3 (5.71)	4.33(5)	0.03801(5)	0.836(3)	1.38(5)	0.0121(5)	0.667(8)	5.71	0.24	0.9999
	5 (5.70)	4.47(7)	0.0565(1)	0.885(5)	1.22(7)	0.017(1)	0.68(1)	5.69	0.21	0.9997
	7 (5.67)	4.4(1)	0.0753(2)	0.820(6)	1.3(1)	0.016(2)	0.66(3)	5.70	0.23	0.9995
	10 (5.65)	3.69(8)	0.1067(2)	0.856(6)	1.95(8)	0.023(1)	0.67(1)	5.64	0.35	0.9996
	15 (5.65)	3.23(2)	0.1458(2)	0.912(3)	2.45(2)	0.0262(3)	0.645(3)	5.68	0.43	0.9998
	20 (5.79)	2.83(4)	0.1272(4)	0.932(7)	2.97(4)	0.0208(5)	0.578(5)	5.80	0.51	0.9996
	25 (5.35)	2.64(4)	0.1285(5)	0.949(7)	2.70(4)	0.0254(6)	0.582(5)	5.35	0.51	0.9995
	30 (5.47)	2.64(6)	0.1028(4)	0.851(8)	2.83(7)	0.0169(6)	0.598(8)	5.47	0.52	0.9996
	35 (5.64)	2.75(7)	0.0767(3)	0.763(7)	2.91(7)	0.0122(4)	0.566(8)	5.66	0.51	0.9996
	36 (5.51)	2.81(7)	0.0707(3)	0.796(7)	2.70(7)	0.0130(5)	0.571(7)	5.51	0.49	0.9994
	40 (5.49)	2.71(6)	0.0722(2)	0.825(6)	2.80(7)	0.0116(4)	0.663(9)	5.51	0.51	0.9998
	45 (5.62)	2.77(7)	0.0584(2)	0.791(7)	2.88(7)	0.0096(3)	0.607(9)	5.65	0.51	0.9997
	50 (5.63)	2.80(7)	0.0511(1)	0.802(6)	2.86(7)	0.0090(3)	0.609(8)	5.66	0.50	0.9997

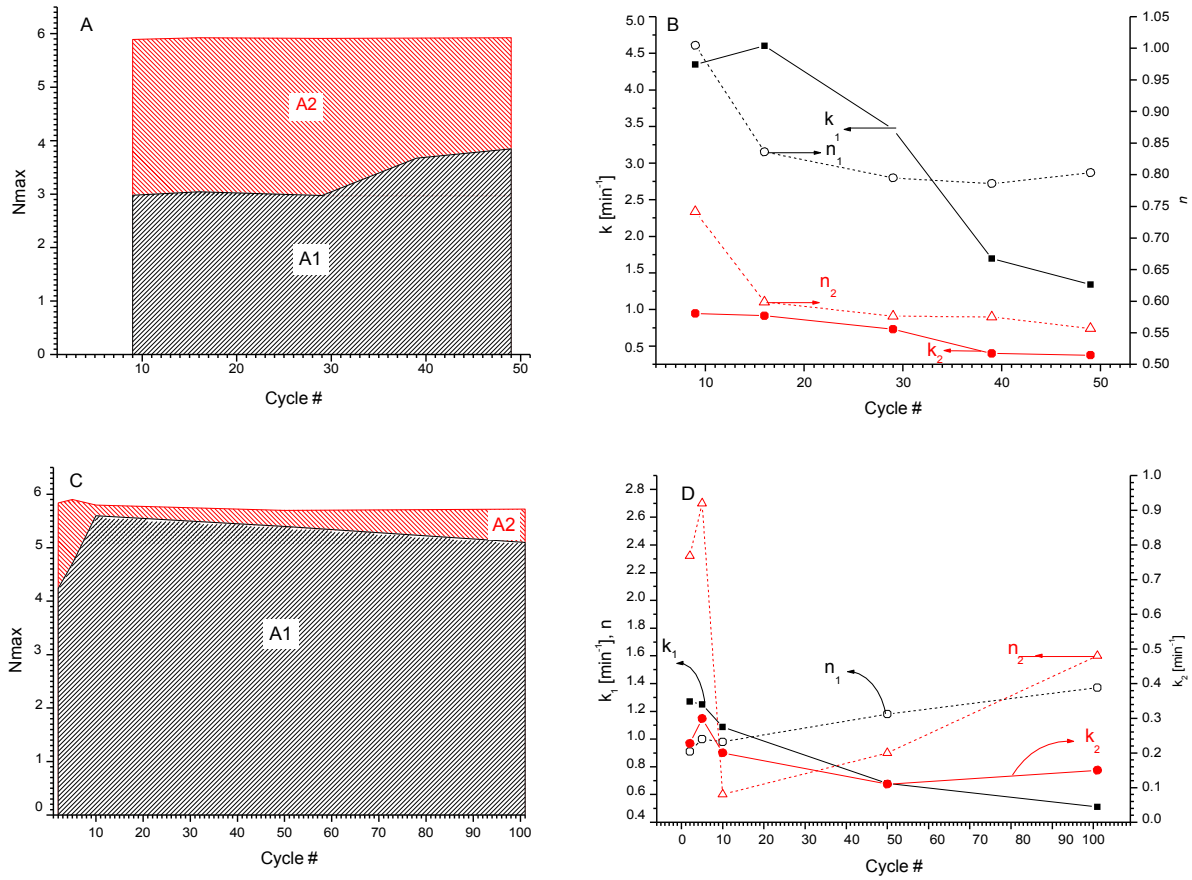

Figure S8.

Changes of kinetic parameters (Eq. 6) of H absorption during cycling for the sample $Mg_{0.9}Ti_{0.1}$ + 5% C at T=200°C (A, B) and 330°C (C, D).

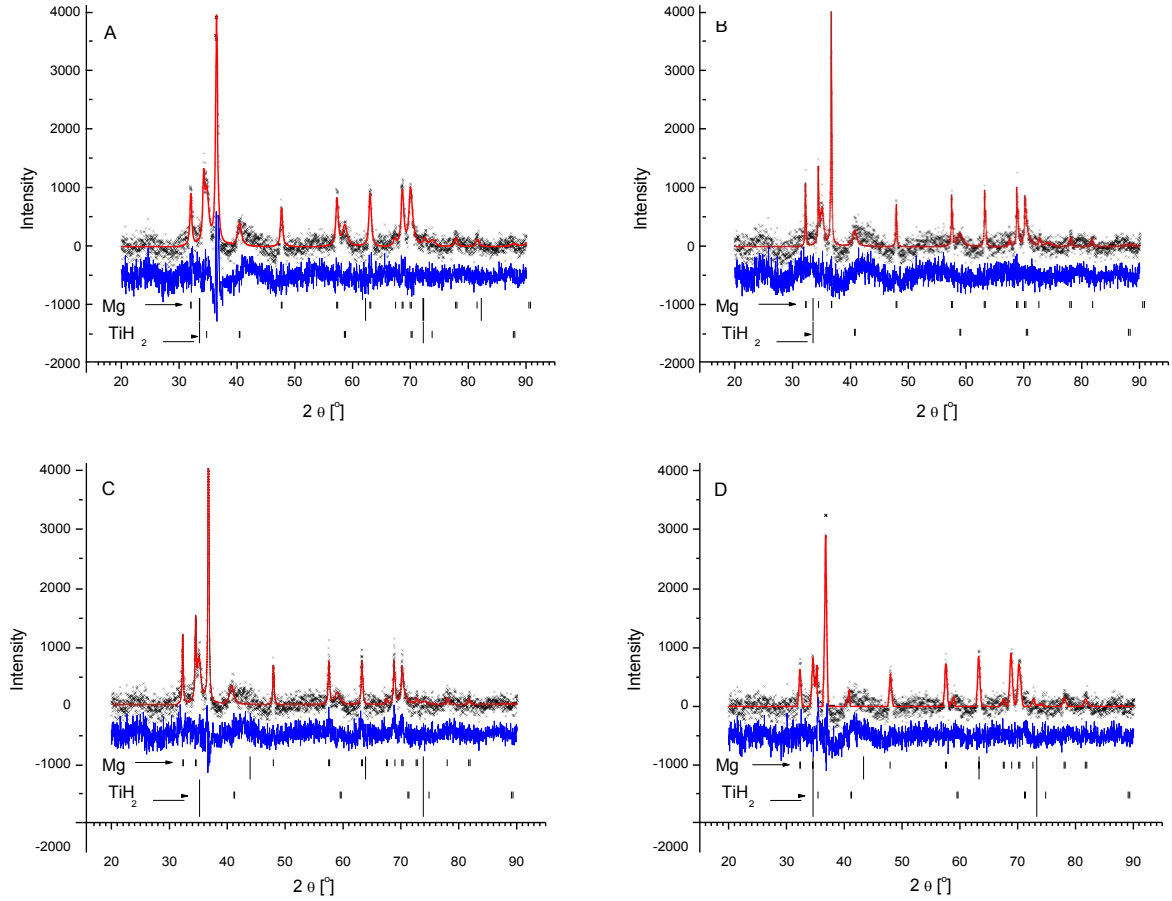

Figure S9.

XRD patterns of dehydrogenated $Mg_{0.9}Ti_{0.1}$ (A, B) and $Mg_{0.9}Ti_{0.1}$ + 5% C(C, D). A, C – before cycling,
B – after 30 H absorption/desorption cycles,
D – after 105 absorption/desorption cycles.
Background subtracted after the refinement.

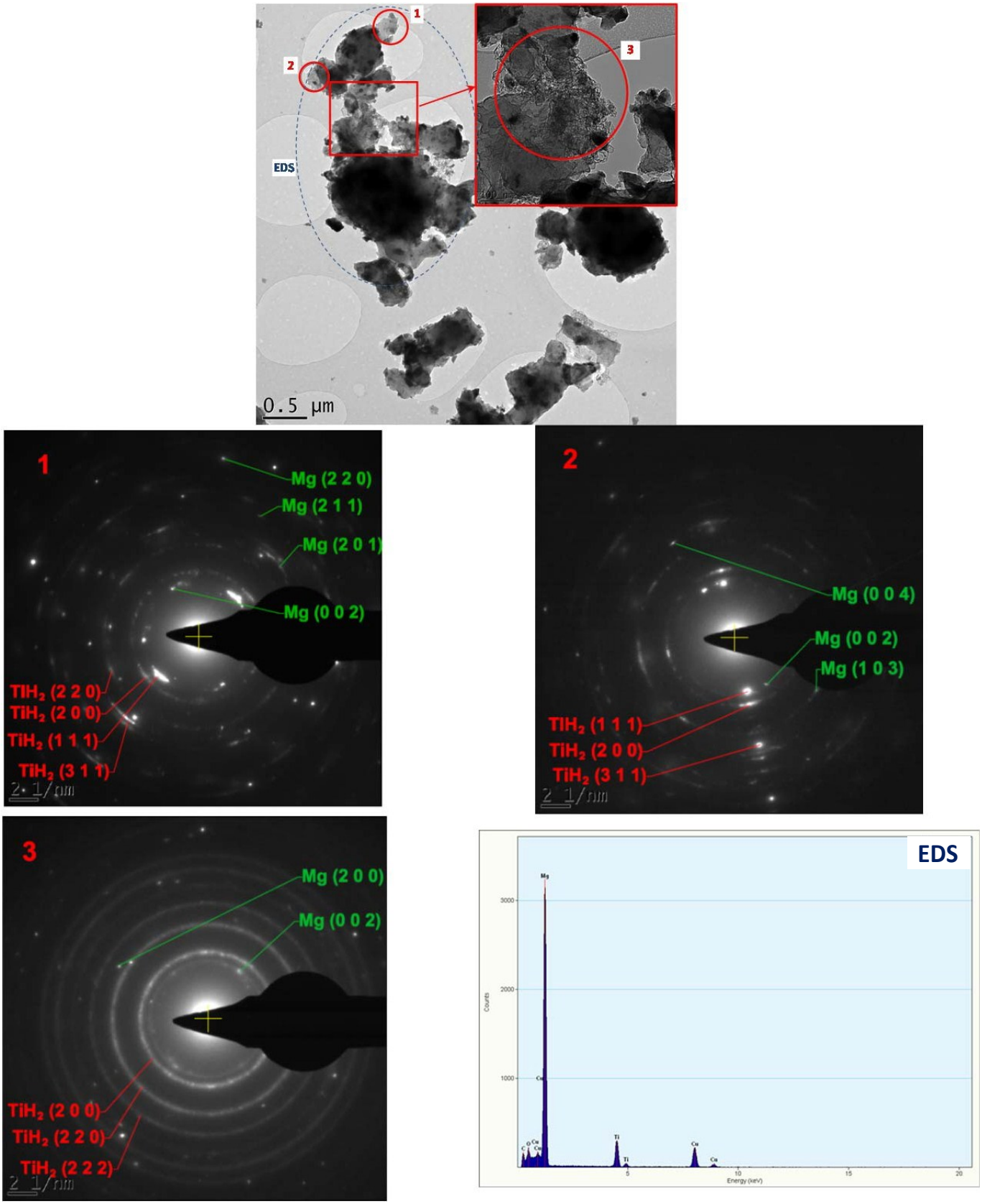

Figure S10.

Top: TEM image of the sample $Mg_{0.9}Ti_{0.1}$. SAD patterns from areas 1, 2 and 3, and EDS[3] are shown below.

[3] The observed Cu peaks in all the EDS spectra originate from the carbon-coated Cu grid, onto which the specimen is placed. This is also the reason of the overestimation of carbon content in the samples derived from the EDS data.

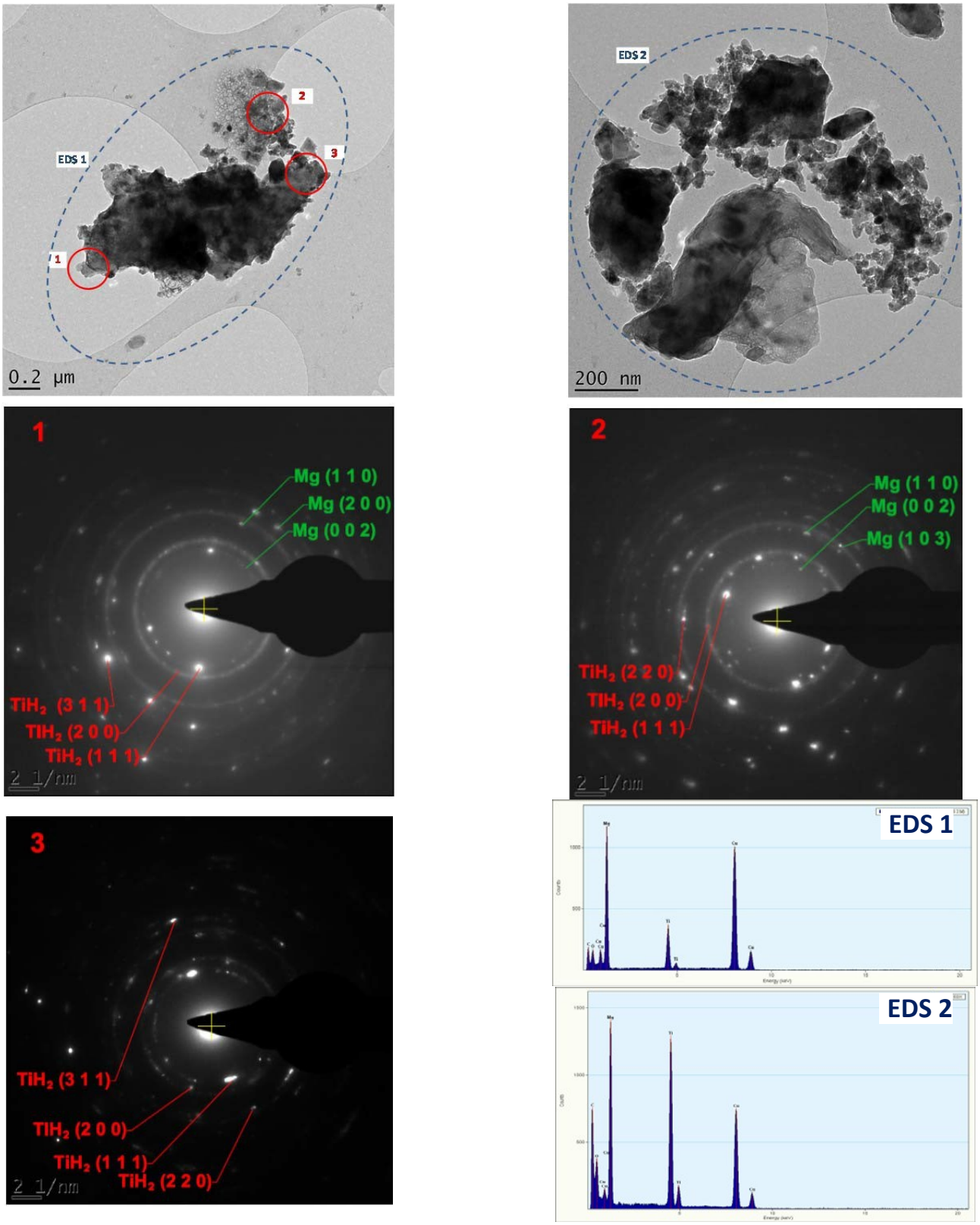

Figure S11. Top: TEM images of the sample $Mg_{0.9}Ti_{0.1}$ (30 cycles). SADP from areas 1, 2 and 3, and EDS[4] are shown below.

[4] In average, the oxygen and carbon contents in the cycled samples determined by EDS were found to be higher than in the non-cycled ones. It allows us to conclude that sample contamination with oxygen and carbon mainly took place during cyclic H absorption / desorption due to traces of O_2, H_2O and hydrocarbons in residual atmosphere.

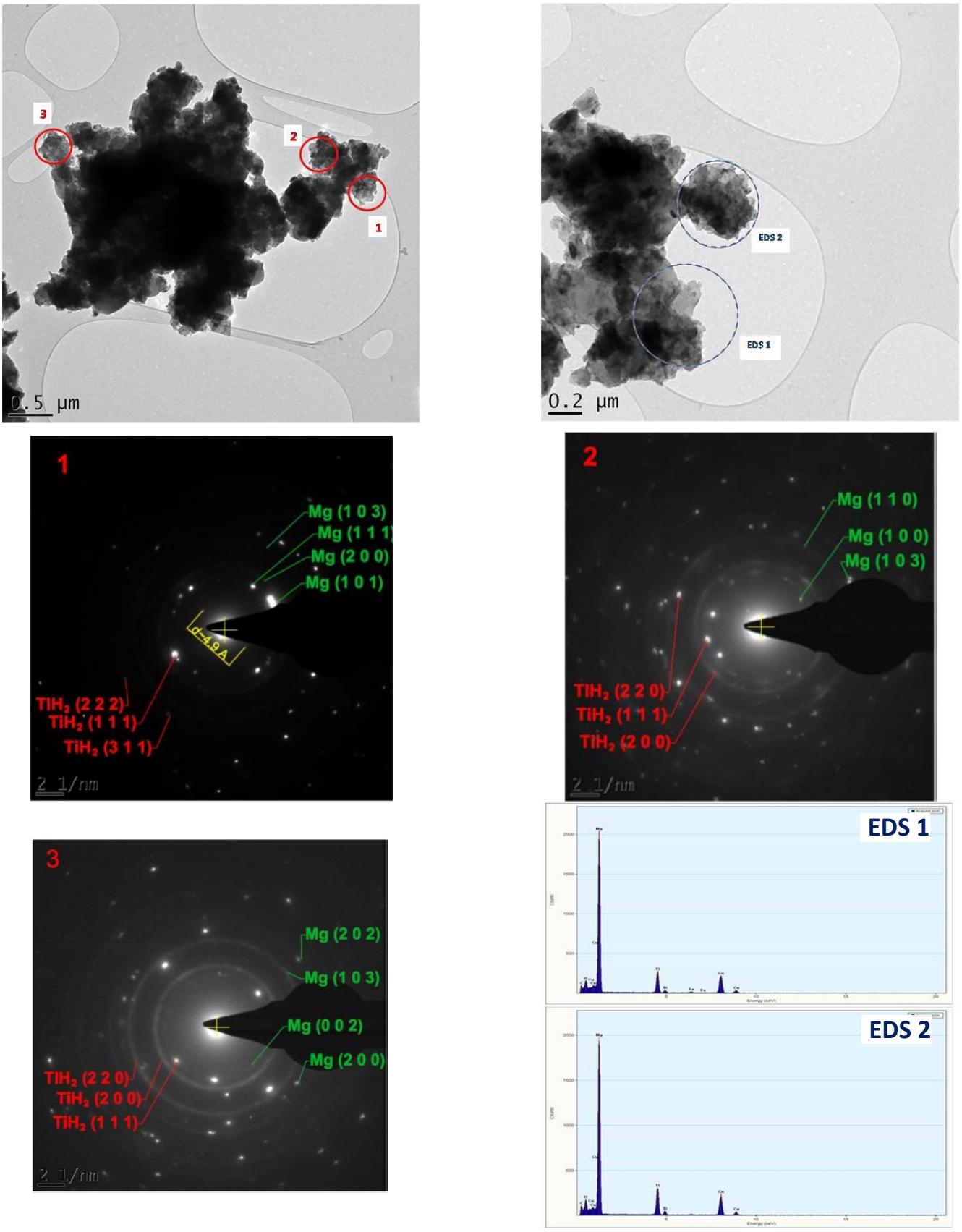

Figure S12.

Top: TEM images of the sample $Mg_{0.9}Ti_{0.1}$ + 5% C. SADP from areas 1, 2 and 3, and EDS are shown below. Two spots with d≈4.9 Å (marked in the pattern 1) may belong to the second-order reflection from (1 0 1) plane of Mg, or (1 1 1) plane of TiH_2.

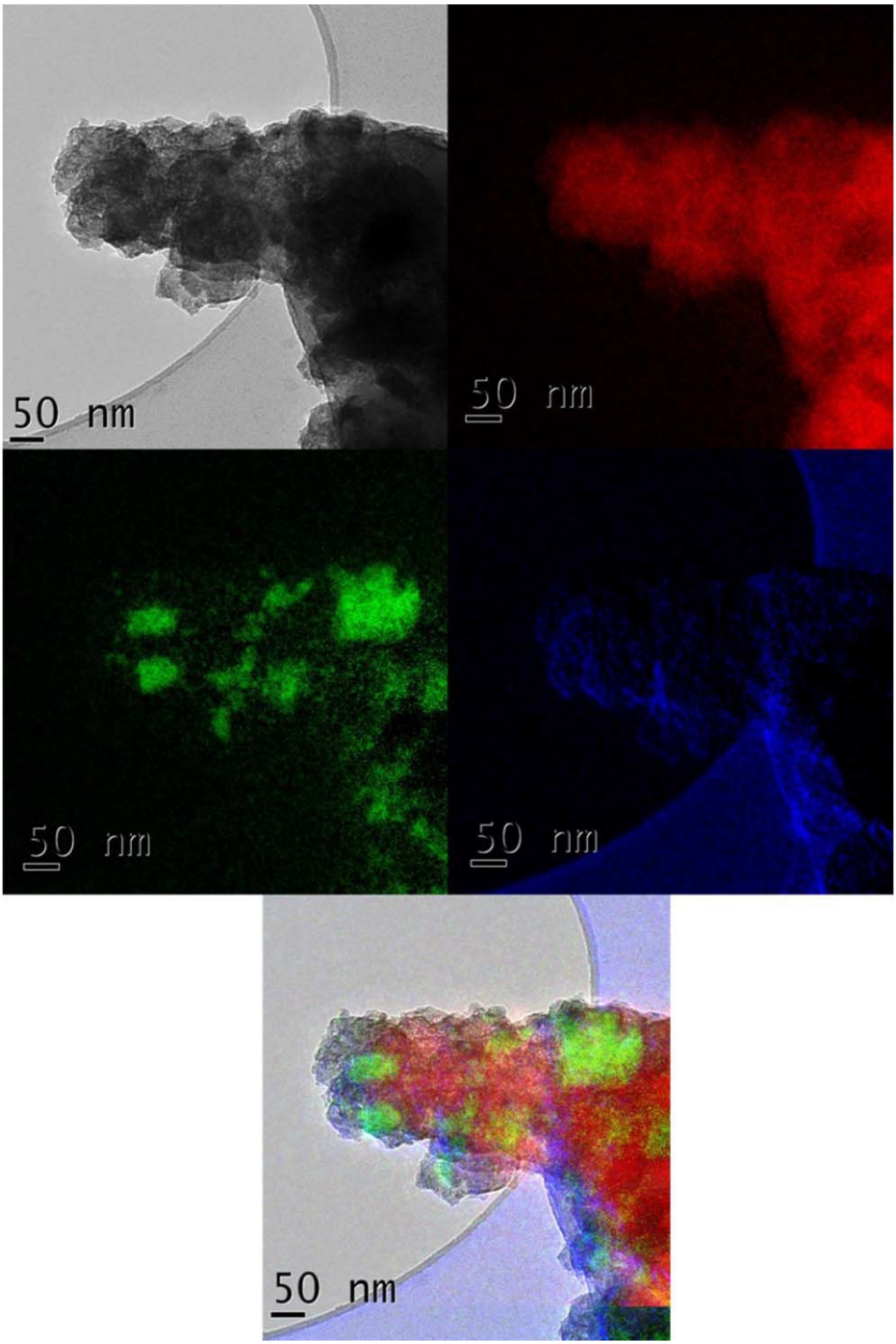

Figure S13.
Top left: filtered image of $Mg_{0.9}Ti_{0.1}$ + 5% C. Top right: Mg map (red), Middle left: Ti map (green). Middle right: C map (blue). Bottom: overlayed map.

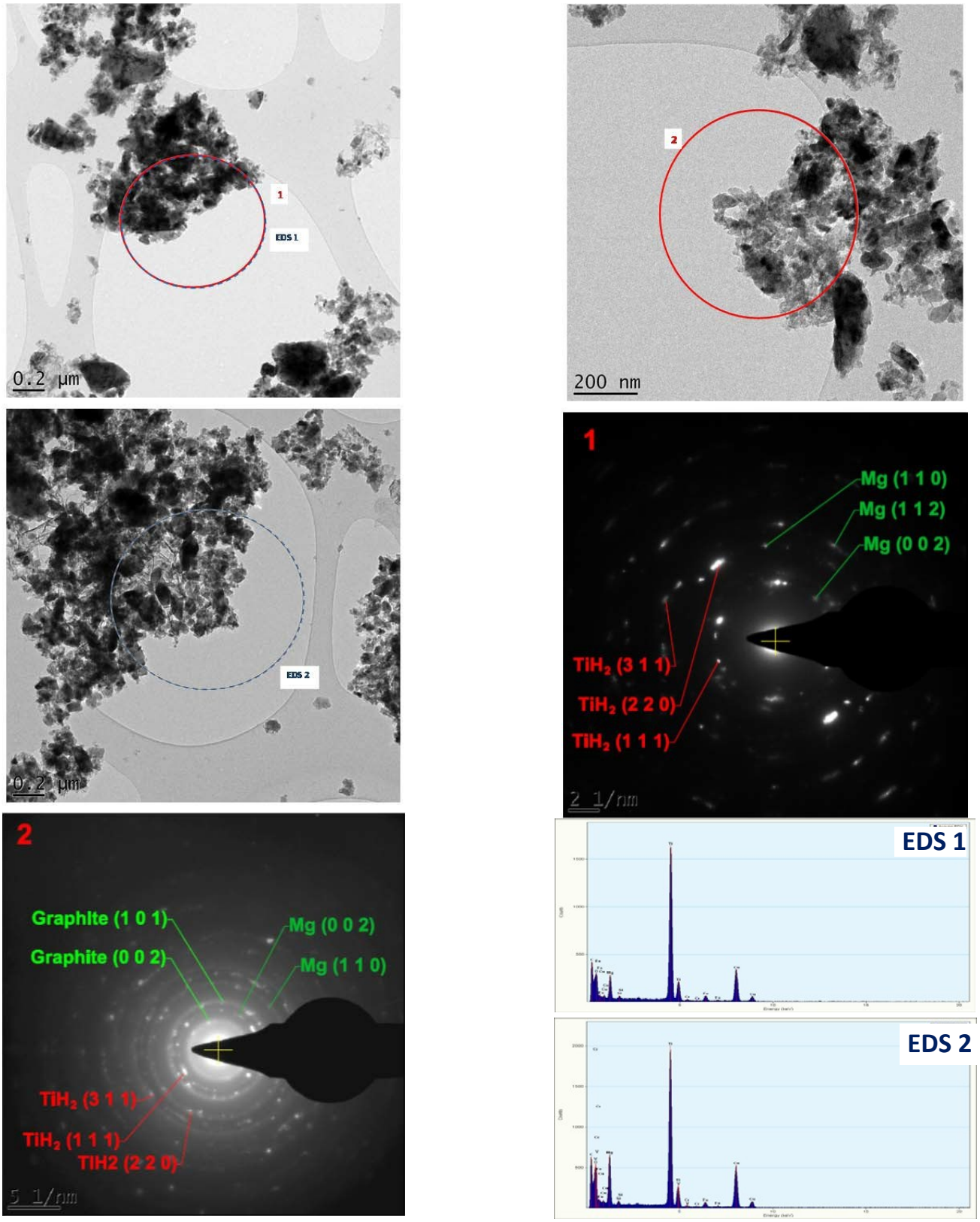

Figure S14.

Top, mid-left: TEM images of the sample $Mg_{0.9}Ti_{0.1}$ + 5% C after 105 H absorption/desorption cycles. SADP from areas 1and 2, and EDS[5] are shown below.

[5] See footnote [4]

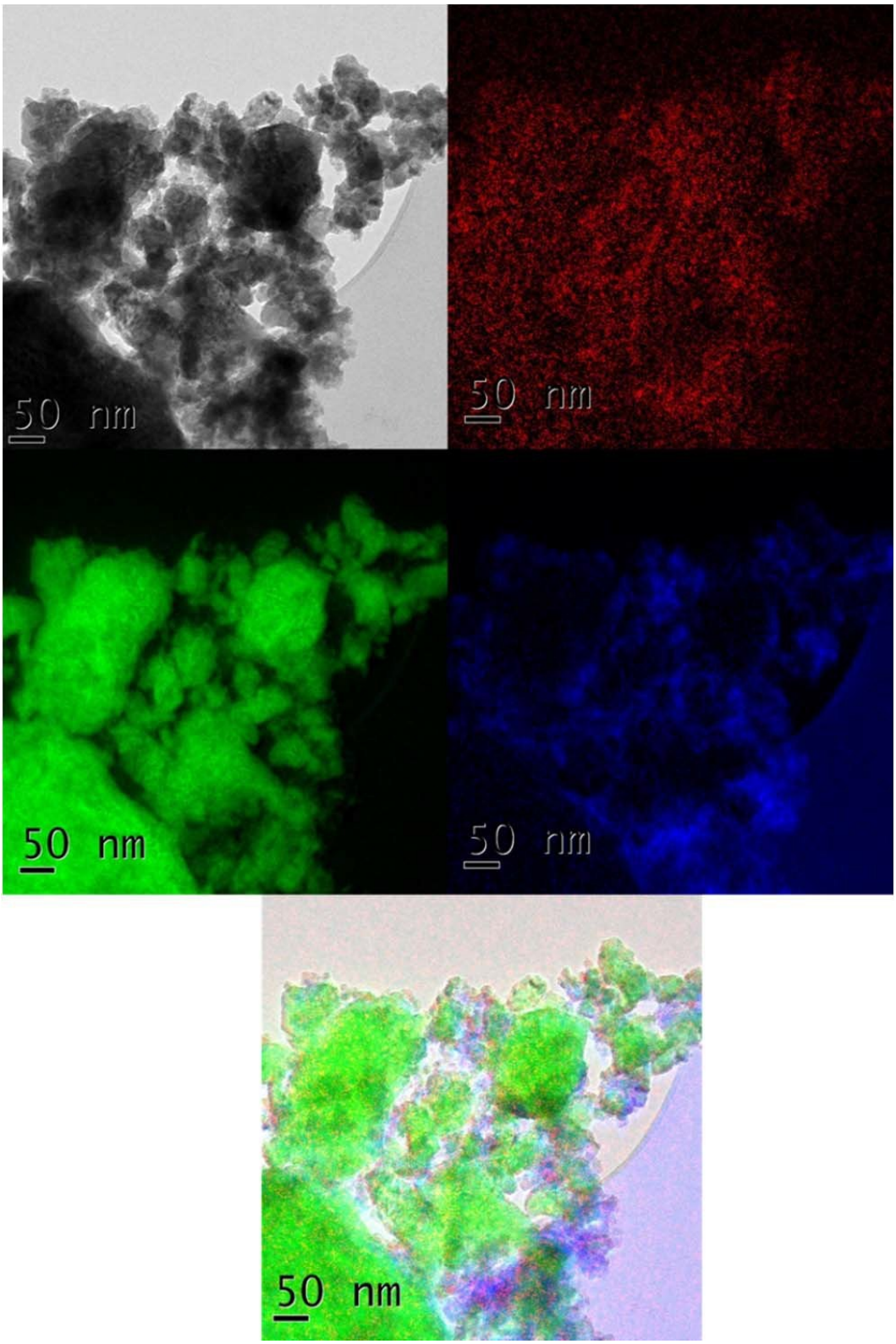

Figure S15.

Top left: filtered image of $Mg_{0.9}Ti_{0.1}$ + 5%C (105 cycles). Top right: Mg map (red), Middle left: Ti map (green). Middle right: C map (blue). Bottom: overlayed map.