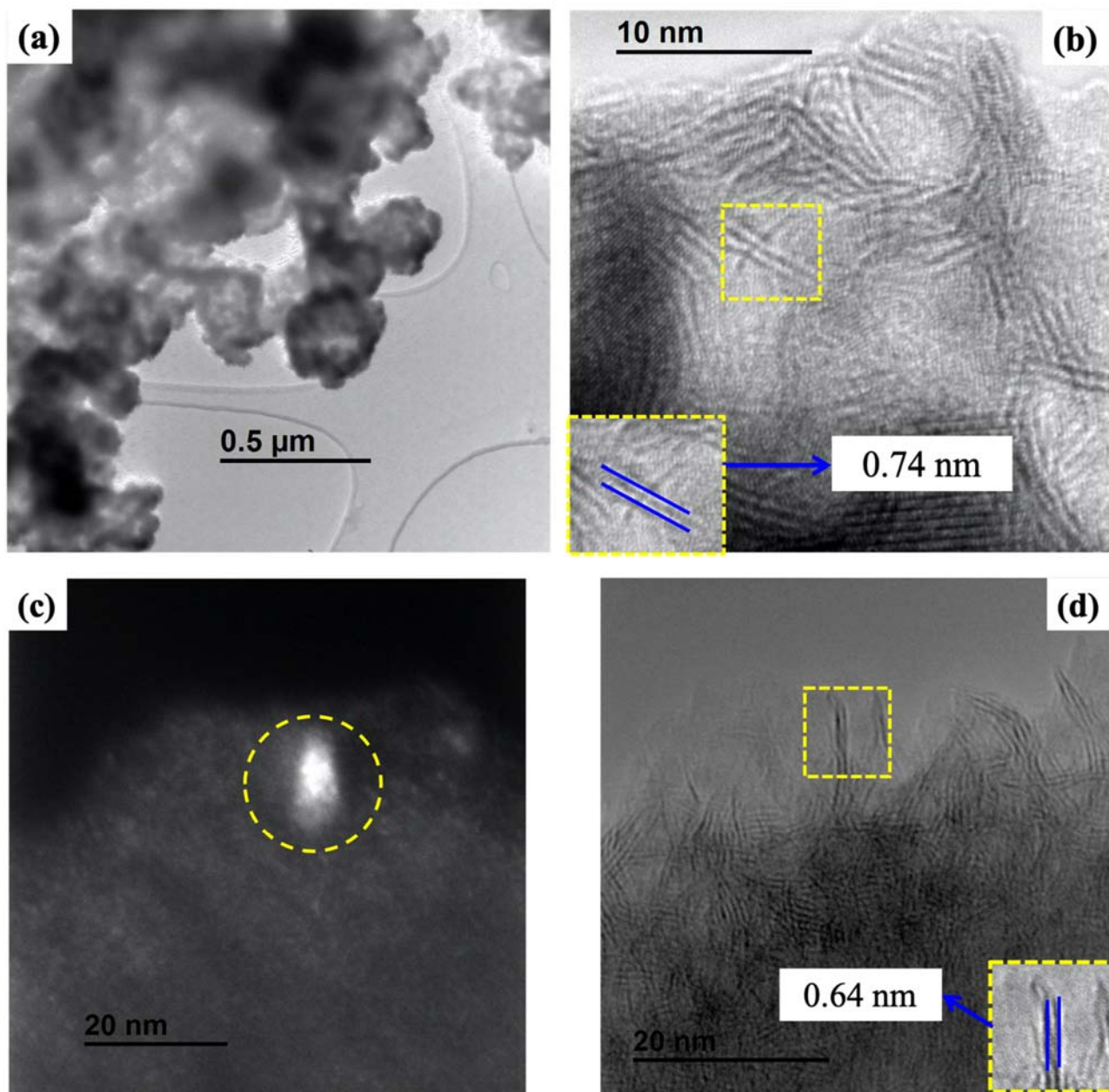


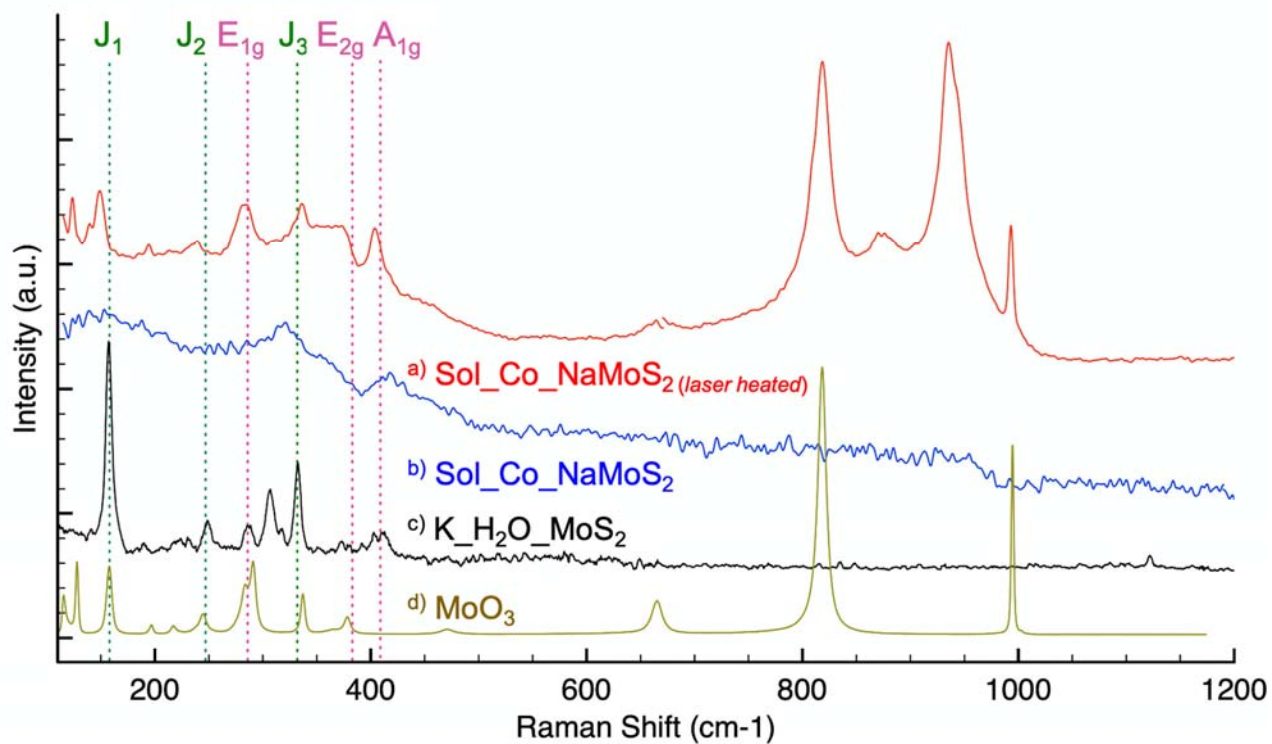
## SUPPORTING INFORMATION

**Table S1. Elemental composition of solvothermal fresh materials and heated at 350°C under H<sub>2</sub>.**

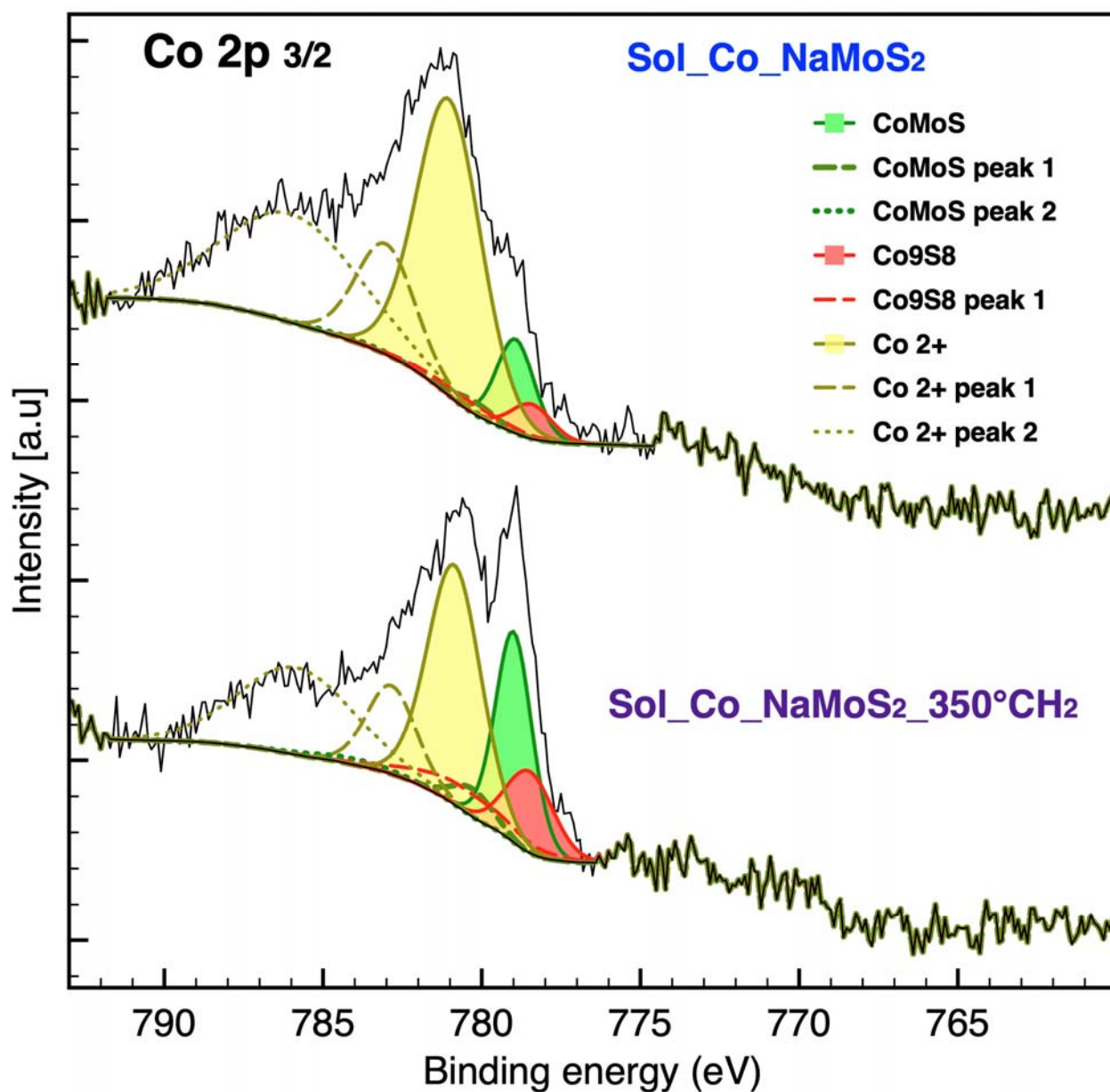
	Atomic % (%wt.)							Total (% wt.)	Empiric formula
	Mo	S	Na	Co	O	C	H		
2H_ATM_MoS <sub>2</sub>	32.4 (58.3)	65 (39.1)	0.0 (0.0)	-	-	-	-	97.4	MoS <sub>2</sub>
Sol_NaMoS <sub>2</sub>	10.6 (47.3)	16.2 (24.1)	1.6 (1.7)	-	15.5 (11.5)	13.5 (7.5)	36.4 (1.7)	93.8	C <sub>1.2</sub> H <sub>3.4</sub> O <sub>1.5</sub> Na <sub>0.2</sub> MoS <sub>1.5</sub>
Sol_Co_NaMoS <sub>2</sub>	8.5 (36.7)	15.1 (21.8)	1.4 (1.4)	4.4 (11.7)	18 (13)	12.7 (6.9)	33 (1.5)	93.1	C <sub>1.5</sub> H <sub>3.9</sub> O <sub>2.1</sub> Co <sub>0.5</sub> Na <sub>0.2</sub> MoS <sub>1.8</sub>
Sol_NaMoS <sub>2</sub> _HDS	22.7 (55.0)	46.0 (37.2)	3.4 (2.0)	-	5.6 (2.3)	5.0 (1.5)	15.7 (0.4)	98.4	C <sub>0.2</sub> H <sub>0.7</sub> O <sub>0.3</sub> Na <sub>0.2</sub> MoS <sub>2.0</sub>
Sol_Co_NaMoS <sub>2</sub> _350°C H <sub>2</sub>	18.8 (40.5)	33.5 (24.2)	3.0 (1.6)	11.5 (15.3)	12.4 (4.5)	1.6 (0.4)	5.7 (0.1)	86.6	C <sub>0.1</sub> H <sub>0.3</sub> O <sub>0.7</sub> Co <sub>0.6</sub> Na <sub>0.2</sub> MoS <sub>1.8</sub>
Sol_Co_NaMoS <sub>2</sub> _HDS	17.8 (43.0)	43.3 (34.9)	2.7 (1.6)	9.6 (14.1)	9.7 (3.9)	4.0 (1.2)	11.9 (0.3)	99.0	C <sub>0.2</sub> H <sub>0.7</sub> O <sub>0.5</sub> Co <sub>0.5</sub> Na <sub>0.2</sub> MoS <sub>2.4</sub>



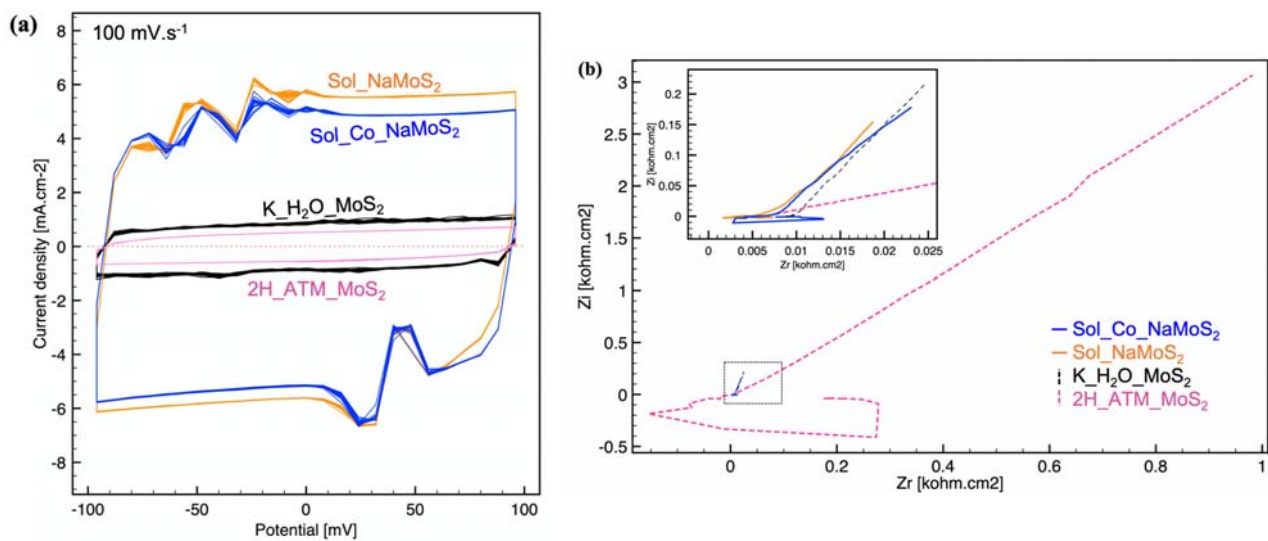
**Figure S1.** Additional TEM images of Sol\_Co\_NaMoS<sub>2</sub>: (a) hollow spheres morphology, (b) magnified edge image of the stacked layers (c) dark-field image of CoS<sub>2</sub> particle, (d) bundles of slabs with the interlayer distance close to that in 2H phase.



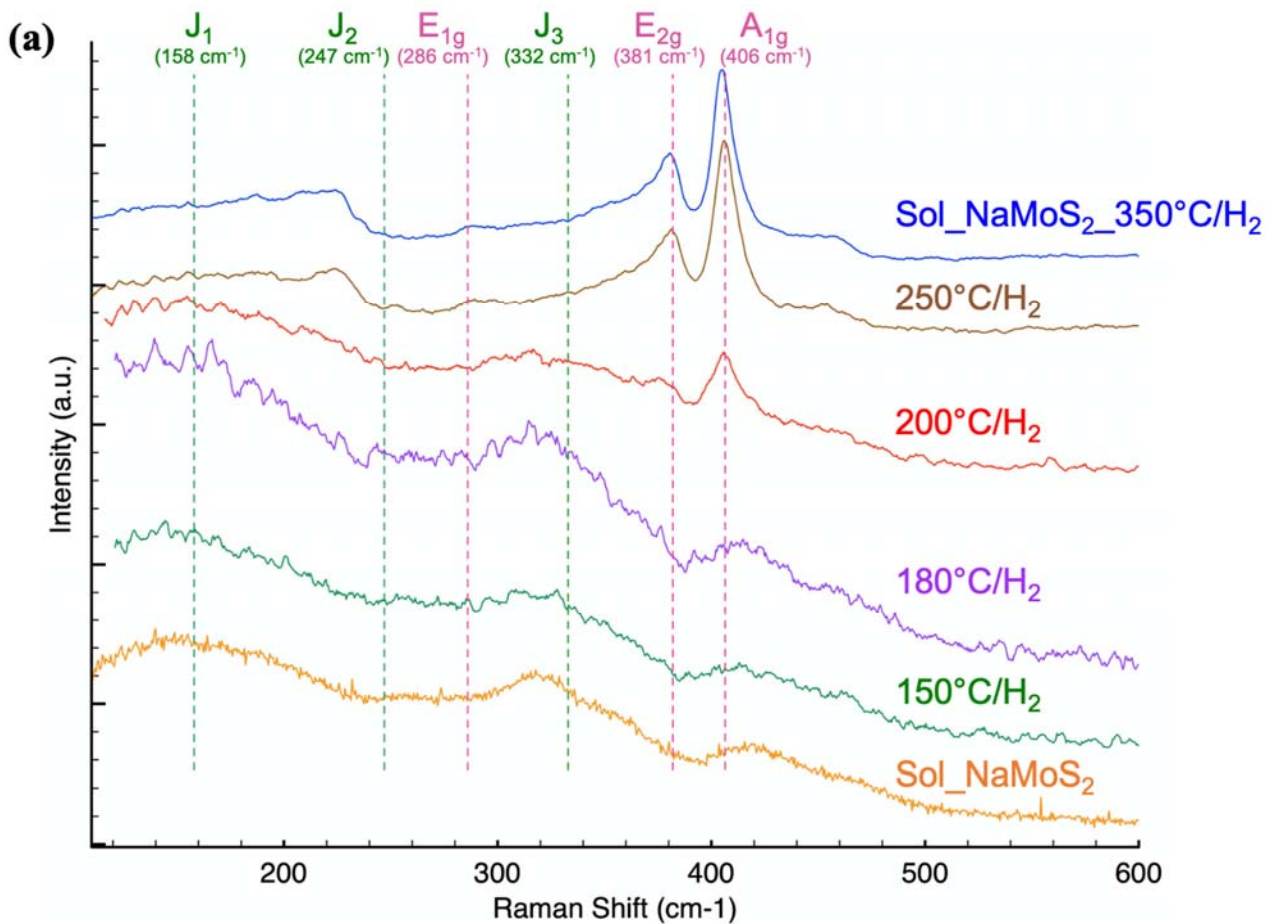
**Figure S2.** Raman spectra of (a) Sol\_Co\_NaMoS<sub>2</sub> with 1 mW power laser (b) initial Sol\_Co\_NaMoS<sub>2</sub> with 0.1 mW power (c) K\_H<sub>2</sub>O\_MoS<sub>2</sub> reference (d) MoO<sub>3</sub>



**Figure S3.** XPS signals of Co 2p region of the fresh solid prepared (Sol\_Co\_NaMoS<sub>2</sub>) and solid heated at 350°C (Sol\_Co\_NaMoS<sub>2</sub>\_350°C).



**Figure S4.** CV curves (a) and EIS plot (b) for Sol\_NaMoS<sub>2</sub> and Sol\_Co\_NaMoS<sub>2</sub> and references K<sub>2</sub>H<sub>2</sub>O\_MoS<sub>2</sub>, 2H\_ATM\_MoS<sub>2</sub> and Pt/C



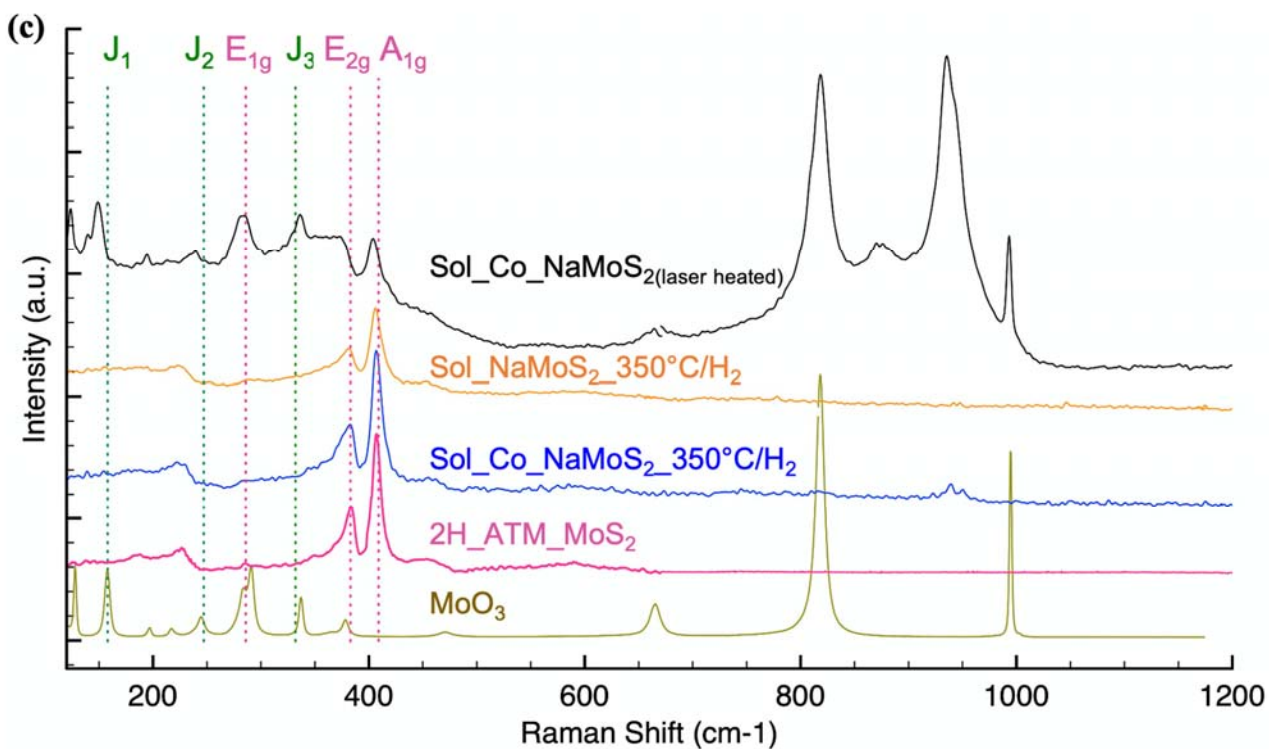
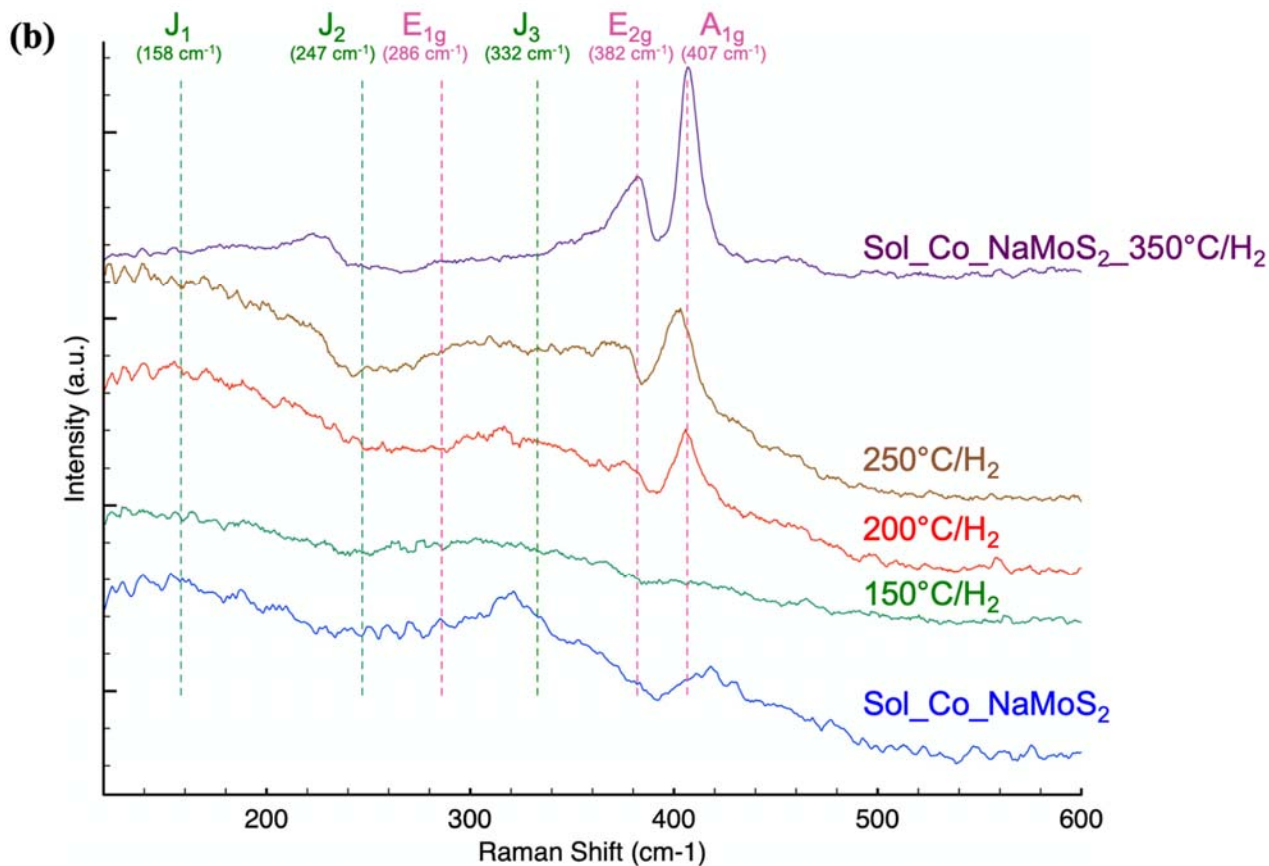
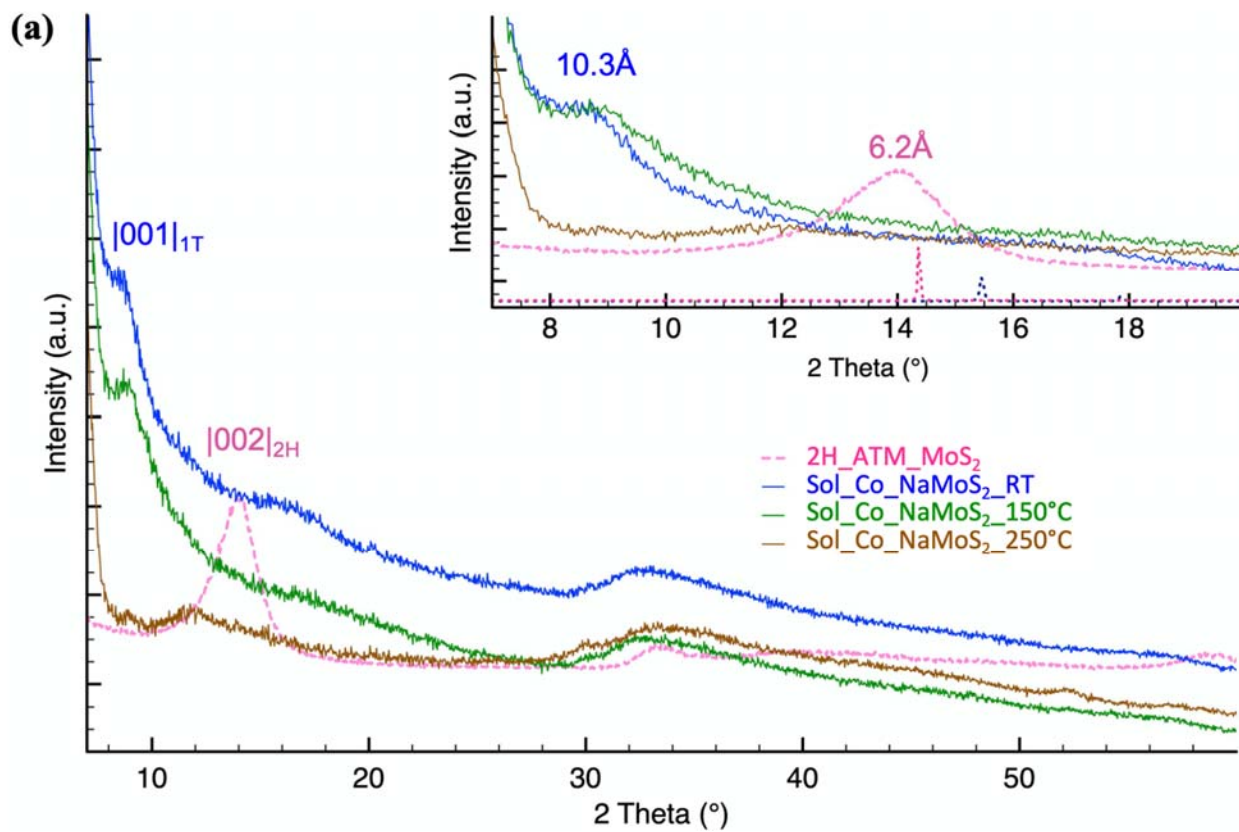
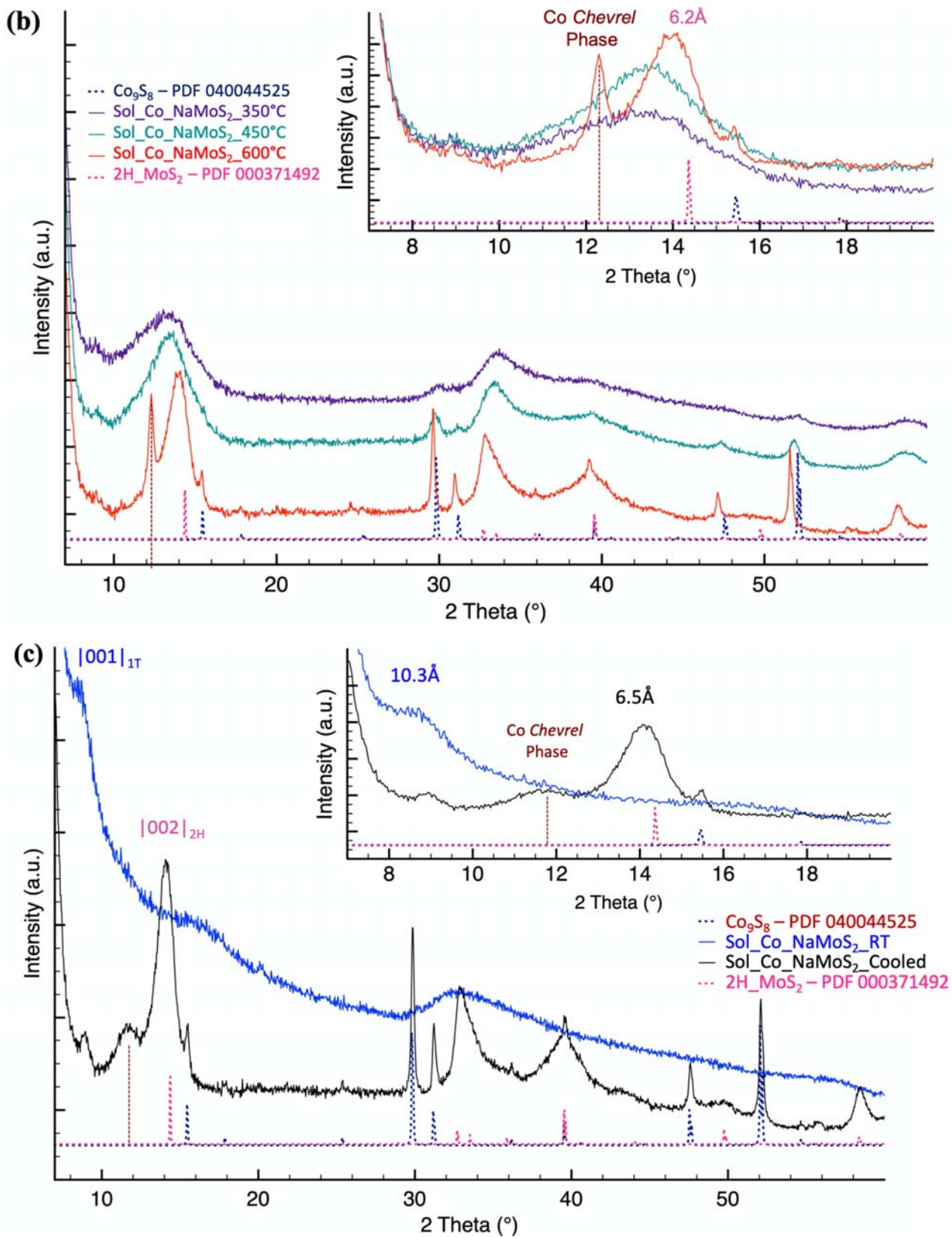


Figure S5. Ex-situ Raman study under H<sub>2</sub> of solvothermal products from RT to 350°C (a,c) Sol\_NaMoS<sub>2</sub>

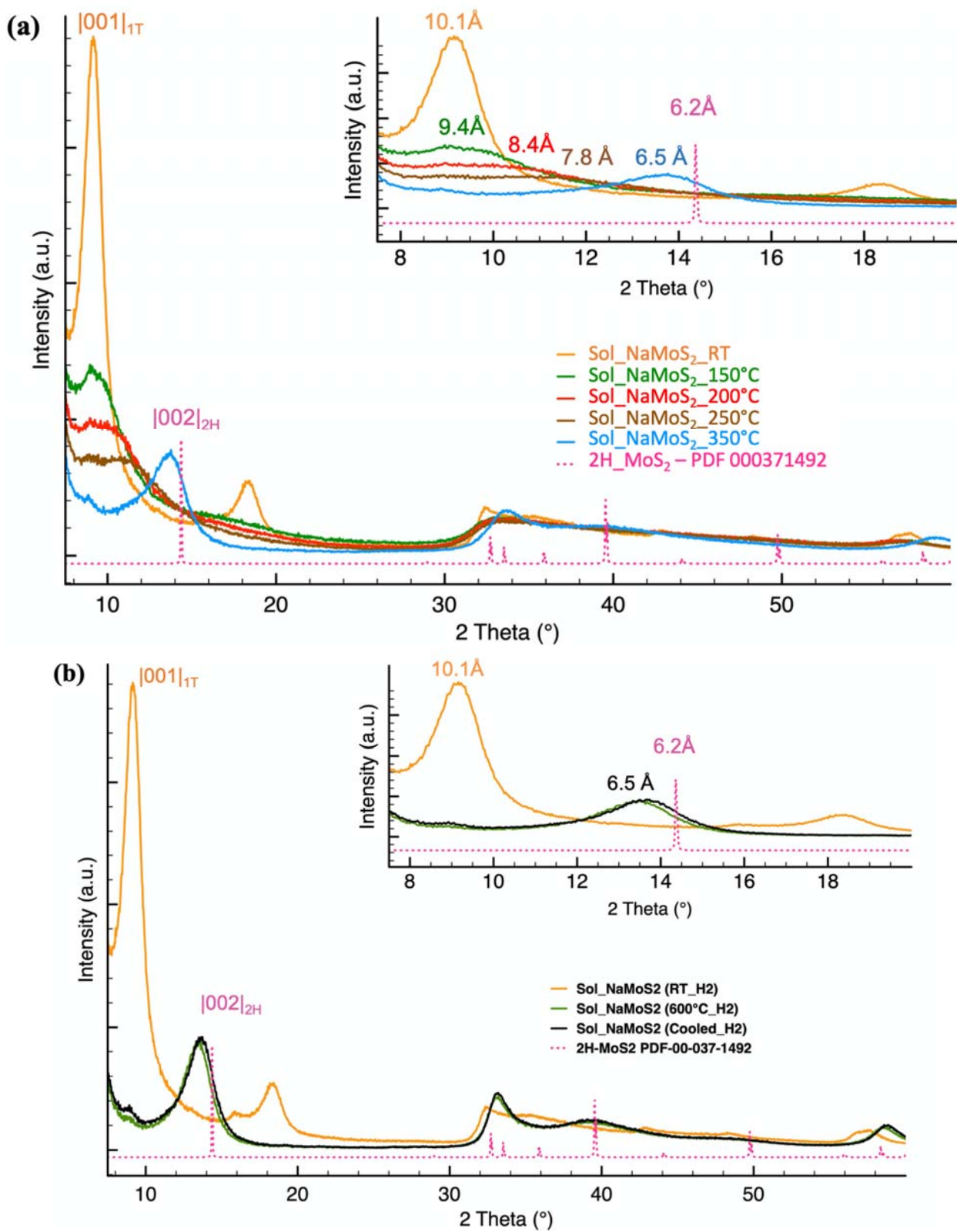
(b,c) Sol\_Co\_NaMoS<sub>2</sub>



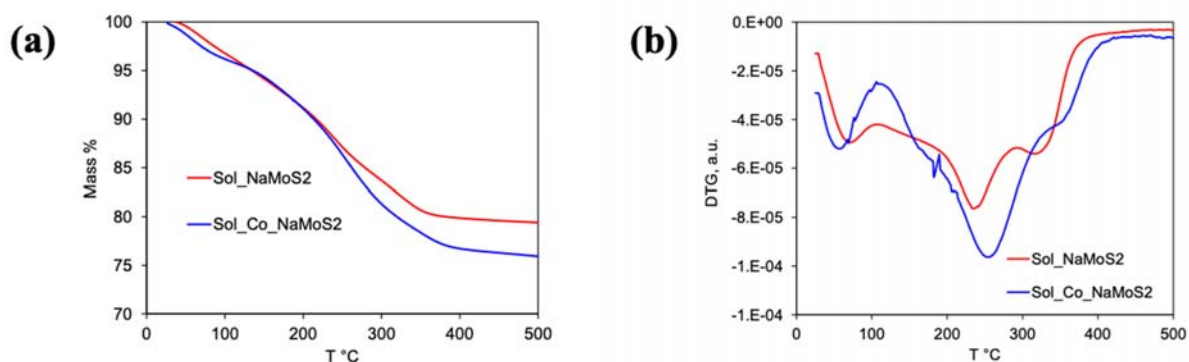


**Figure S6.** XRD patterns Sol\_Co\_NaMoS<sub>2</sub> detected upon heating under H<sub>2</sub> flow (a) from 25°C to 250°C. (b) 300°C to 600°C then (c) cooled to room temperature.





**Figure S7.** XRD patterns Sol\_NaMoS<sub>2</sub> detected upon heating under H<sub>2</sub> flow (a) from 25°C to 350°C. (b) heated to 600°C and cooled to room temperature.



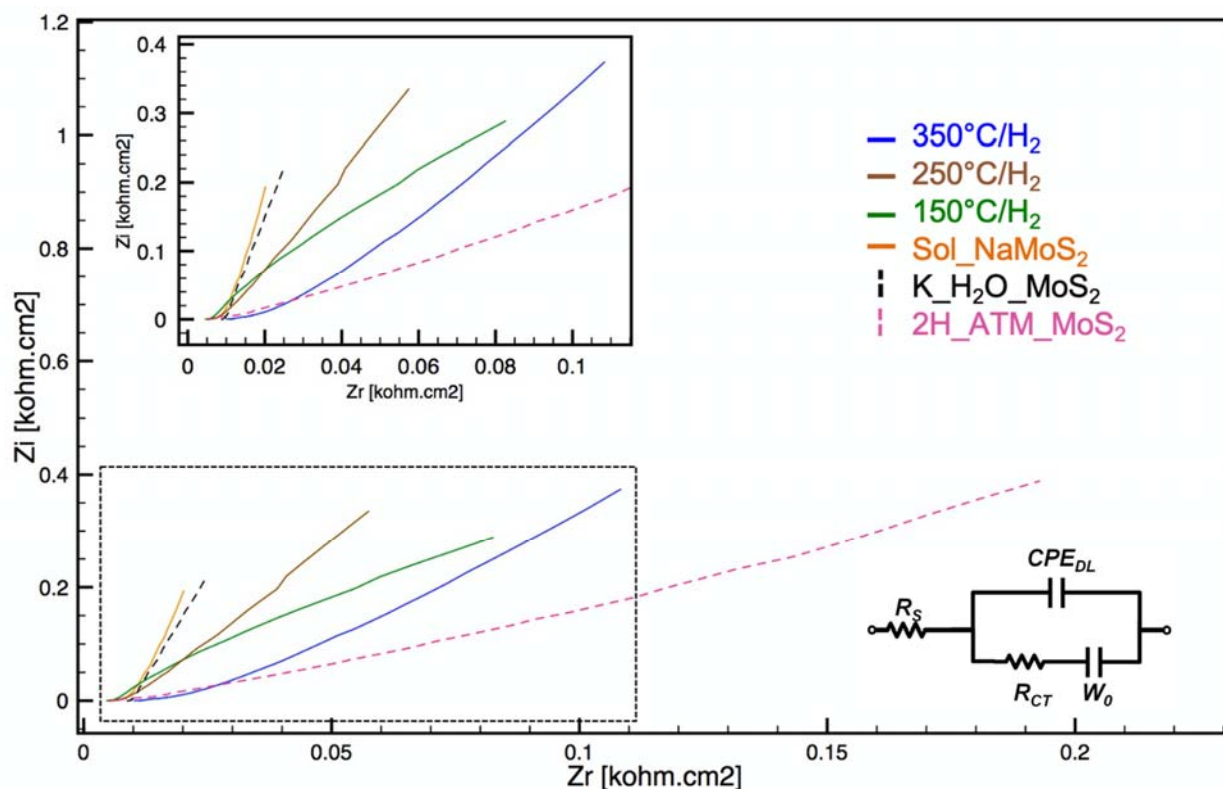
**Figure S8.** TG (a) and DTG (b) curves for the solvothermal solids heated under  $N_2$

**Table S2.** HER properties of the solvothermal products heated under  $H_2$  at different temperatures and references

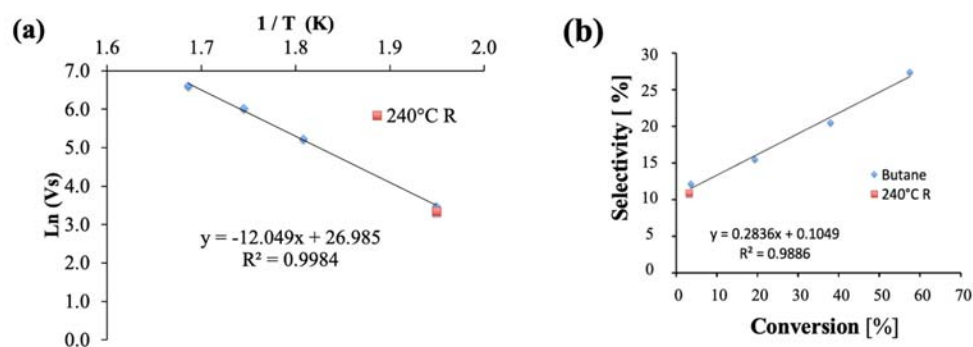
HER measurement	Sol_NaMoS <sub>2</sub>	150°C/H <sub>2</sub>	250°C/H <sub>2</sub>	350°C/H <sub>2</sub>	K_H <sub>2</sub> O_MoS <sub>2</sub>	2H_ATM_MoS <sub>2</sub>
OP <sub>-10mA.cm<sup>-2</sup></sub> [mV]	-207	-281	-277	- 334	- 232	- 355
Tafel slope [mV/dec]	50	56	82	113	72	124
ECSA [m <sup>2</sup> /g]	198	42	51	31	33	17
N <sub>2</sub> Adsorption [m <sup>2</sup> /g]	90	-	-	15	17	49
R <sub>D</sub> [Ω]	14	-	272	511	16	975

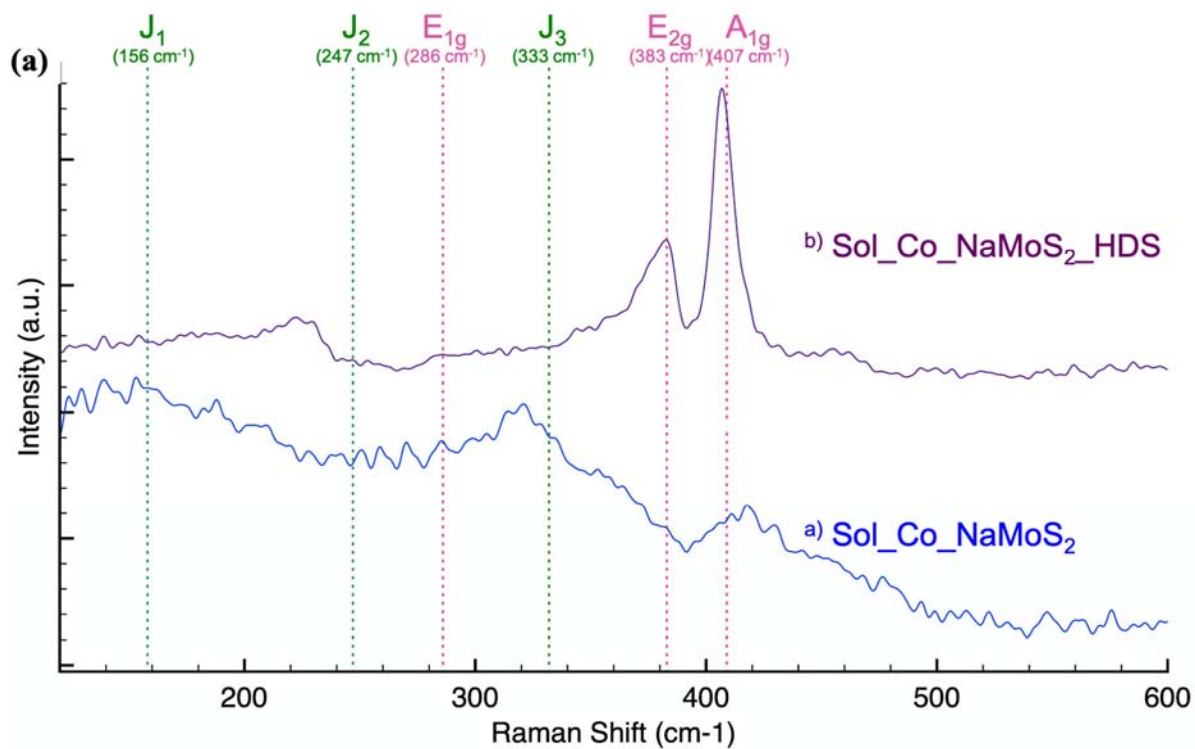
HER measurement	Sol_Co_NaMoS <sub>2</sub>	150°C/H <sub>2</sub>	250°C/H <sub>2</sub>	350°C/H <sub>2</sub>	PPC_CoMoS	Pt / C
OP <sub>-10mA.cm<sup>-2</sup></sub> [mV]	-191	-269	-267	- 280	- 297	- 49
Tafel slope [mV/dec]	55	64	78	71	76	36
ECSA [m <sup>2</sup> /g]	211	47	36	12	12	-
R <sub>D</sub> [Ω]	17	-	349	1121	1146	-



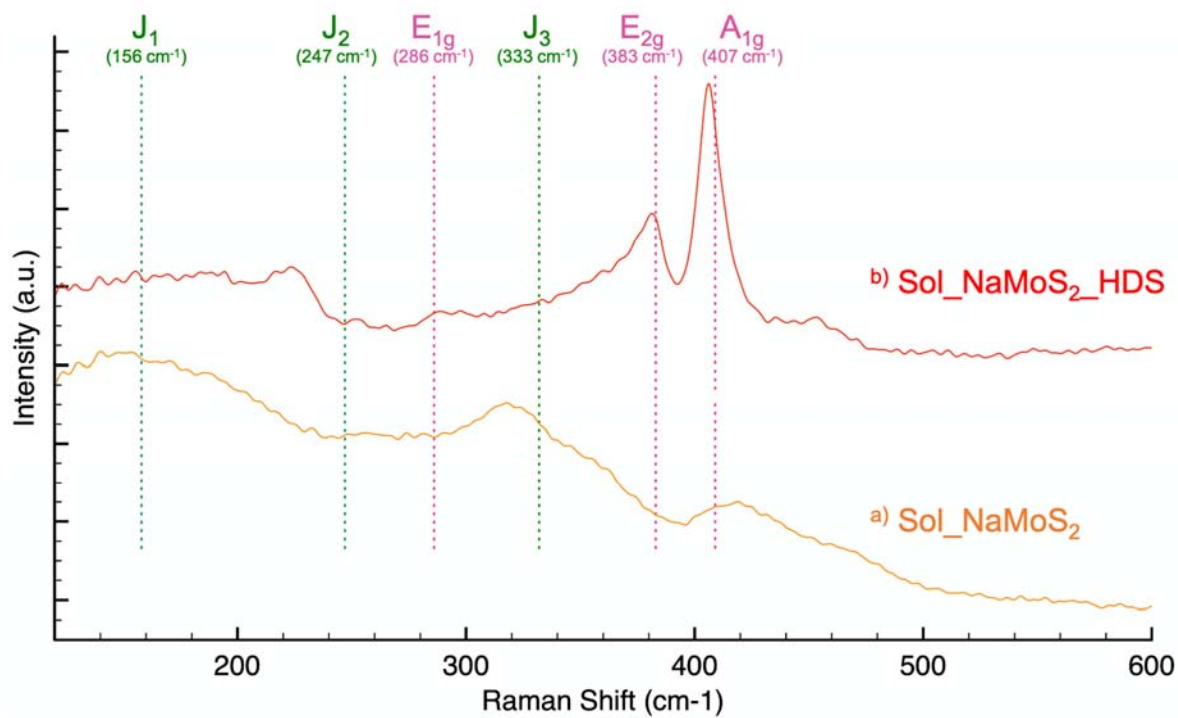
**Figure S9.** EIS plots of the initial and heated in H<sub>2</sub> Sol\_NaMoS<sub>2</sub> samples vs. references. Inset – equivalent scheme to determine R<sub>CT</sub>



**Fig S10.** Arrhenius plot of thiophene HDS rate of the Sol\_Co\_NaMoS<sub>2</sub> catalyst (a) and butane selectivity vs. conversion (b). Activation energy is 25±2 Kcal/mol. 240 °C R and red mark designates retour point at 240 °C.



**Fig S11.a.** Raman spectra of solvothermal product: (a) before HDS test Sol\_Co\_NaMoS<sub>2</sub> and (b) after HDS test Sol\_Co\_NaMoS<sub>2</sub>\_HDS.

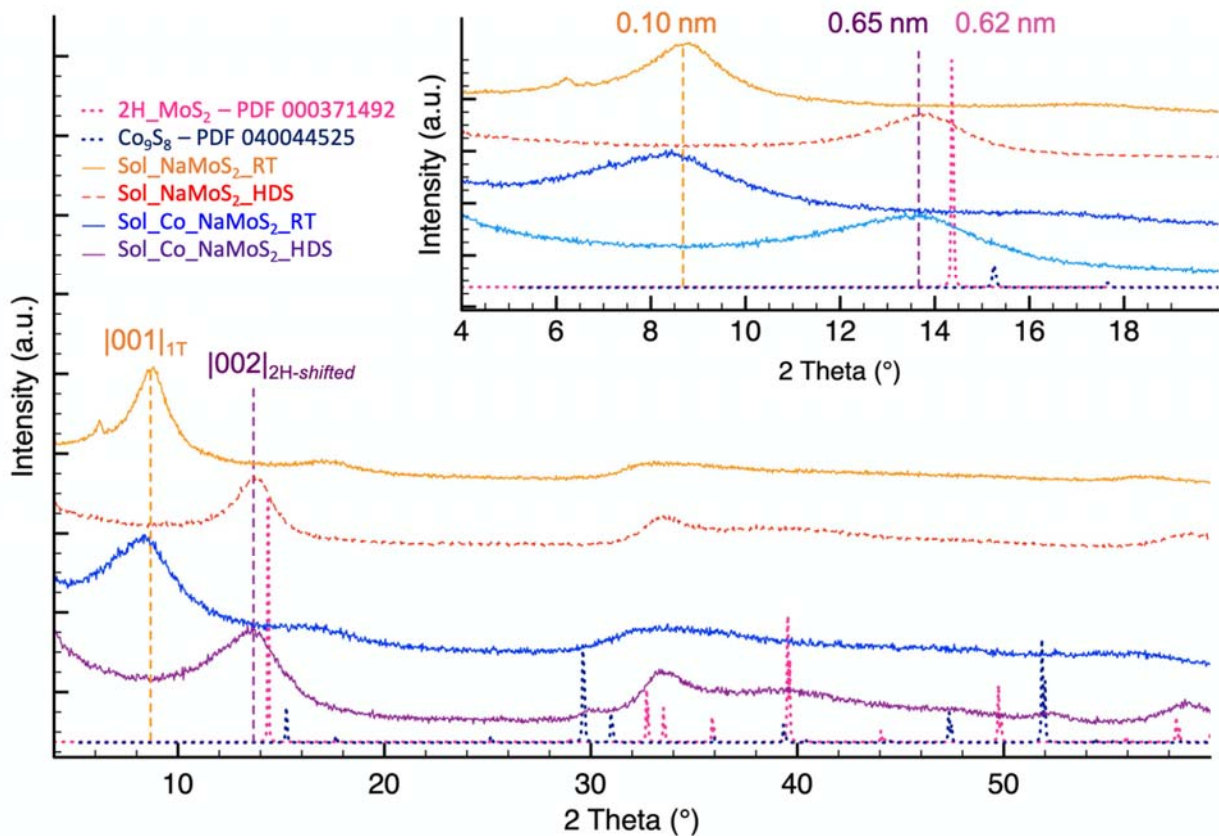


**Fig S11.b.** Raman spectra of solvothermal product: (a) before HDS test Sol\_NaMoS<sub>2</sub> and (b) after HDS test Sol\_NaMoS<sub>2</sub>\_HDS.

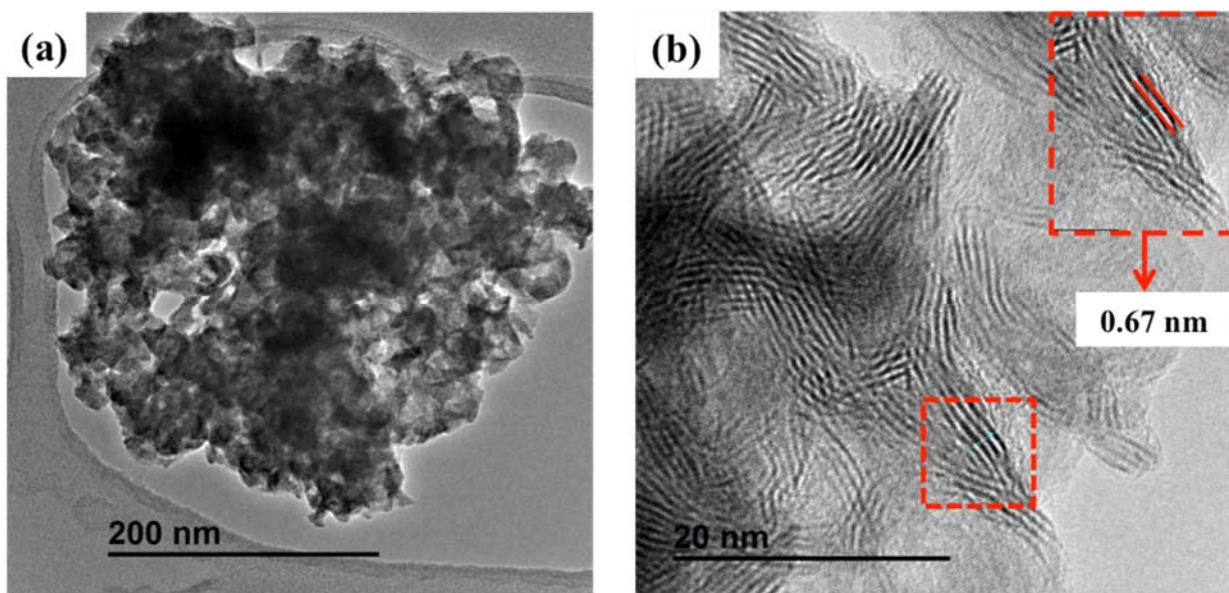
**Table S3.** HER properties of Sol\_NaMoS<sub>2</sub> and Sol\_Co\_NaMoS<sub>2</sub> before and after HDS test and references 2H\_ATM\_MoS<sub>2</sub> and Pt/C

HER measure	Sol_Co_NaMoS <sub>2</sub>	Sol_Co_NaMoS <sub>2</sub> _HDS	PPC_CoMoS	Pt / C
OP <sub>-10mA.cm<sup>-2</sup></sub> [mV]	- 191	-176	- 297	- 49
Tafel slope [mV/dec]	55	83	76	36
ECSA [m <sup>2</sup> /g]	190	24	12	-
N <sub>2</sub> Adsorption [m <sup>2</sup> /g]	212	73	38	-

HER measure	Sol_NaMoS <sub>2</sub>	Sol_NaMoS <sub>2</sub> _HDS	2H_ATM_MoS <sub>2</sub>	Pt / C
OP <sub>-10mA.cm<sup>-2</sup></sub> [mV]	- 207	-254	- 355	- 49
Tafel slope [mV/dec]	50	117	124	36
ECSA [m <sup>2</sup> /g]	171	16	17	-
N <sub>2</sub> Adsorption [m <sup>2</sup> /g]	63	25	49	-



**Fig. S12.** XRD of the solvothermal products before and after HDS test



**Fig S13.** TEM images of Sol\_NaMoS<sub>2</sub> after HDS test (a) sheet-like morphology (b) magnified edge image of the stacked layers