

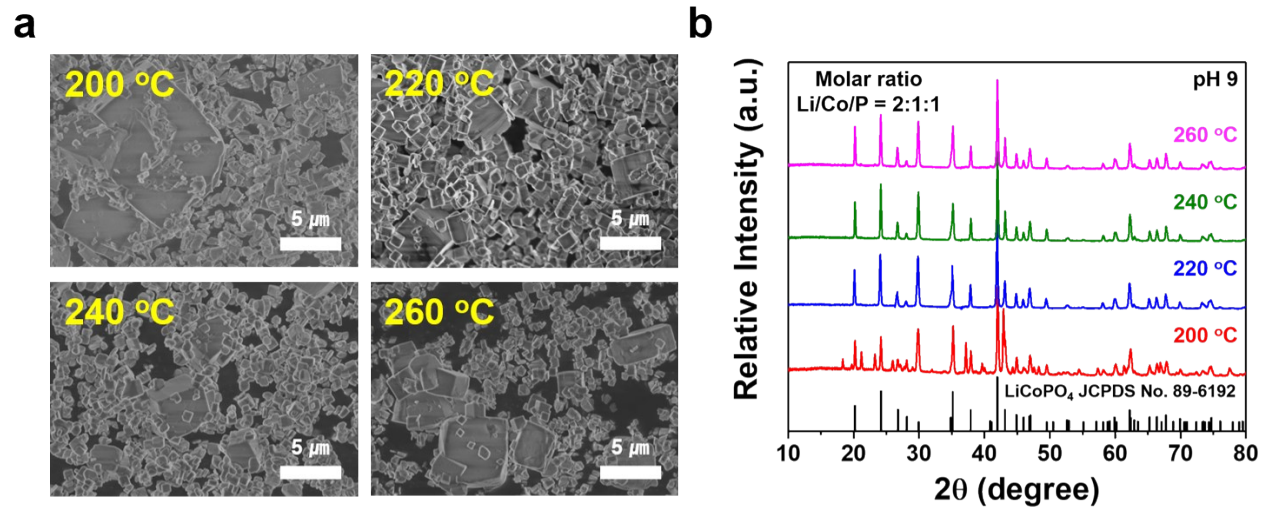
## Supplementary Information

# Surface and bulk defect formation during hydrothermal synthesis of LiCoPO<sub>4</sub> crystals and their electrochemical implications

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**Figure S1. Morphology and phase characterizations of hydrothermally synthesized LCP (HT-LCP) samples for 6 hours at different temperatures via (a) SEM and (b) XRD. (The concentration of  $\text{CoSO}_4$  and  $\text{H}_3\text{PO}_4$  is fixed at 0.4 M).**

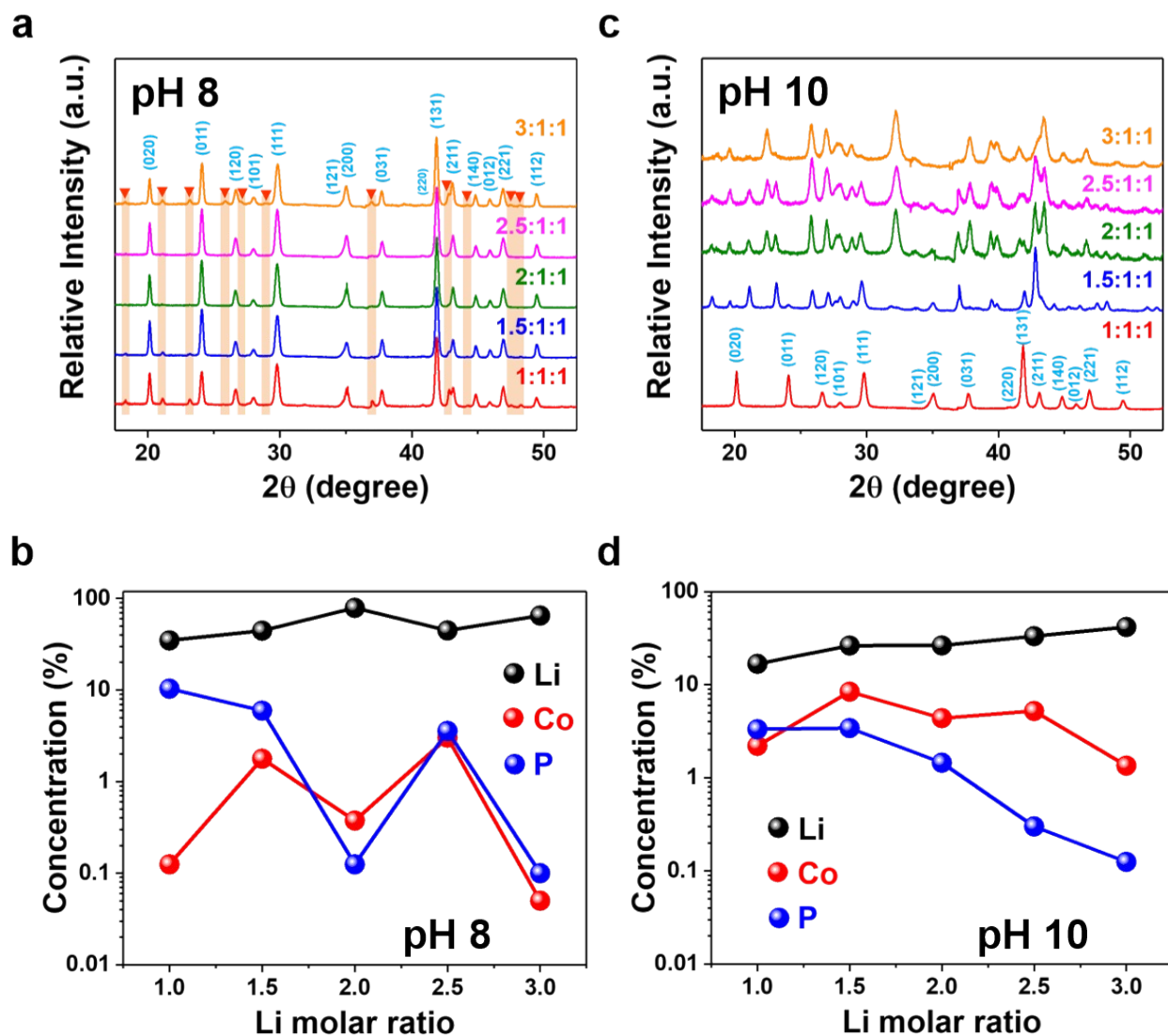
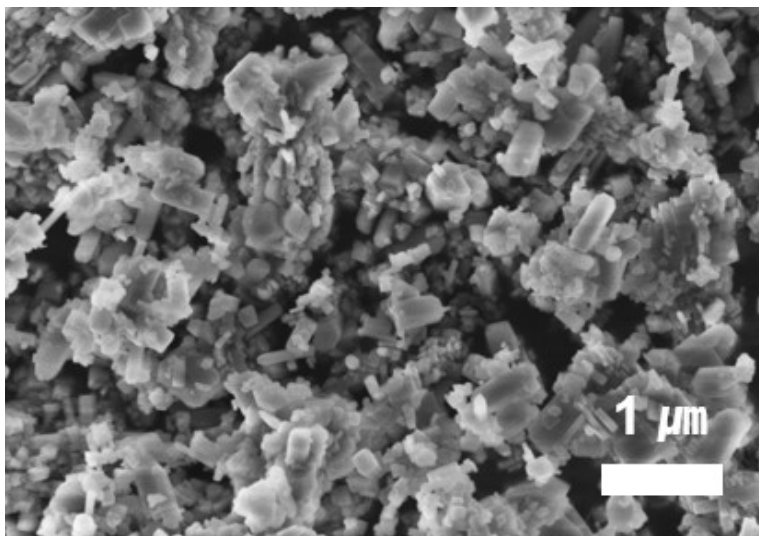


Figure S2. Phase and elemental comparison of HT-LCP samples from the precursor solutions with different Li/Co/P molar ratio at (a-b) pH 8 and (c-d) 10 (The concentration of  $\text{CoSO}_4$  and  $\text{H}_3\text{PO}_4$  is fixed at 0.4 M).

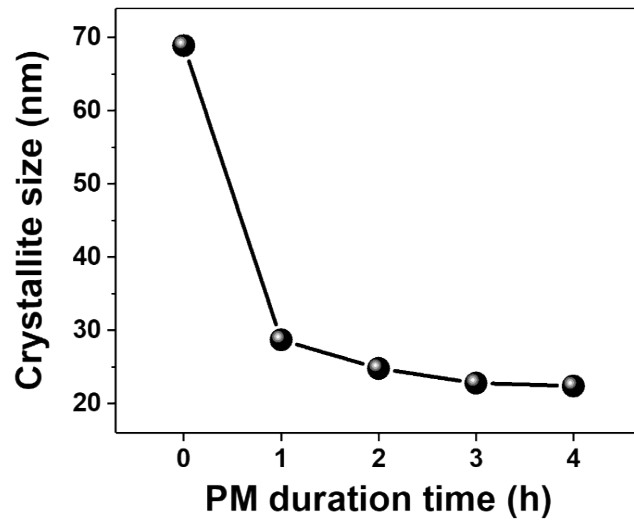
**Table S1. pH value variations before and after HT-synthesis.**

<b>Li/Co/P Molar ratio</b>	<b>pH 8</b>		<b>pH 9</b>		<b>pH 10</b>	
	<b>Before</b>	<b>After</b>	<b>Before</b>	<b>After</b>	<b>Before</b>	<b>After</b>
1:1:1	8	6.1	9	9.17	10	10
1.5:1:1	8	5.04	9	9.1	10	10.14
2:1:1	8	4.97	9	9.07	10	10.16
2.5:1:1	8	6.26	9	9.38	10	9.96
3:1:1	8	8.75	9	9.36	10	10

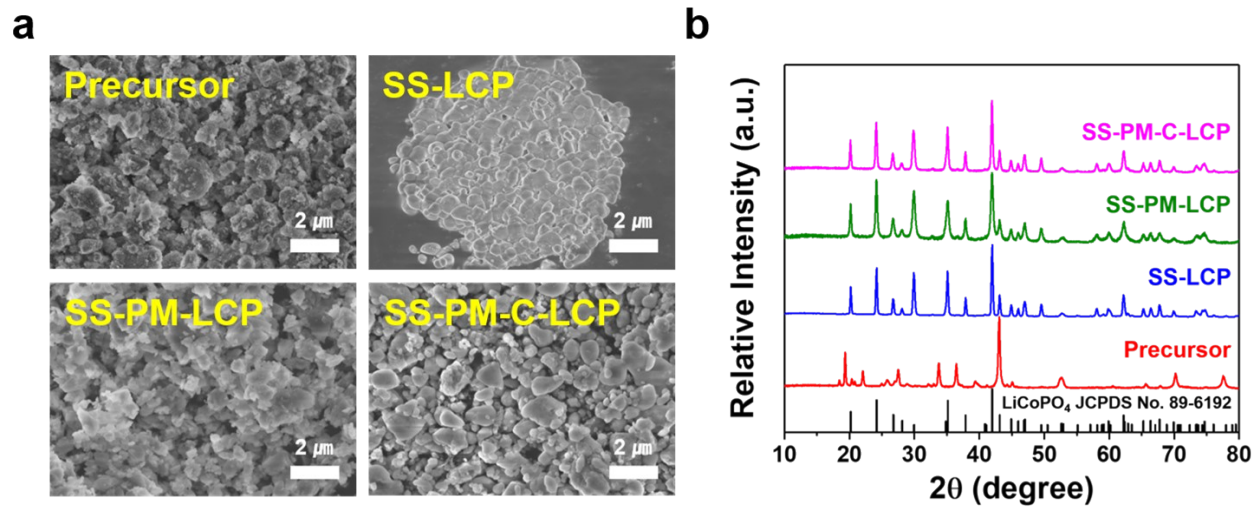
**(The concentration of CoSO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> is fixed at 0.4 M)**



**Figure S3. Morphology of LCP nanocrystals from the precursor solutions with the stoichiometric ratio 1:1:1 (Li:Co:P) at pH 10.**



**Figure S4. Crystallite size calculated based on Rietveld refinement with the increasing PM duration time.**



**Figure S5.** Morphology and phase characterizations of LCP samples obtained by solid-state reaction (SS-LCP) and post-synthesis treatments (SS-PM-LCP and SS-PM-C-LCP) via (a) SEM and (b) XRD.

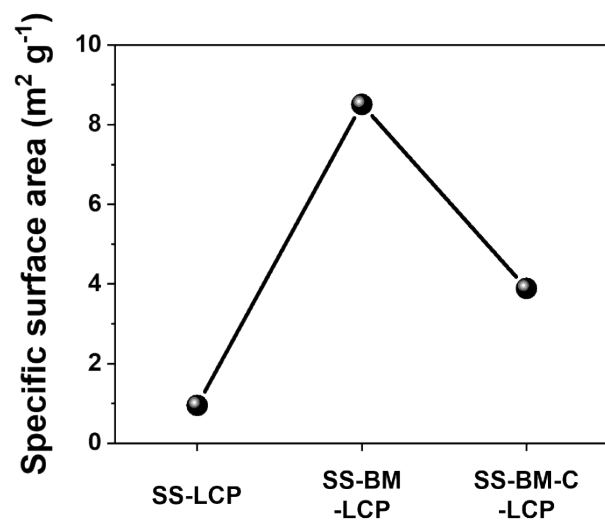
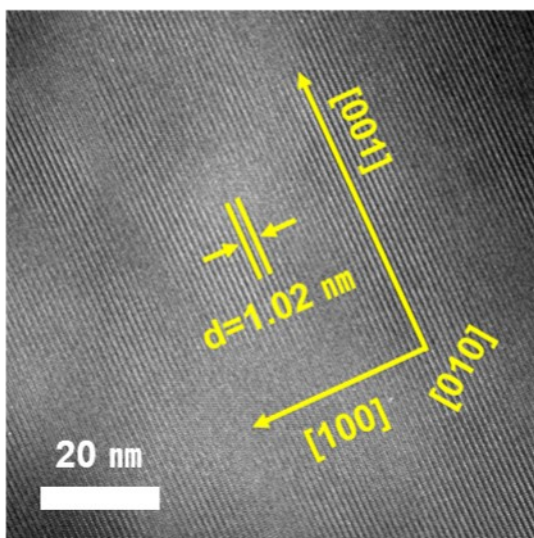


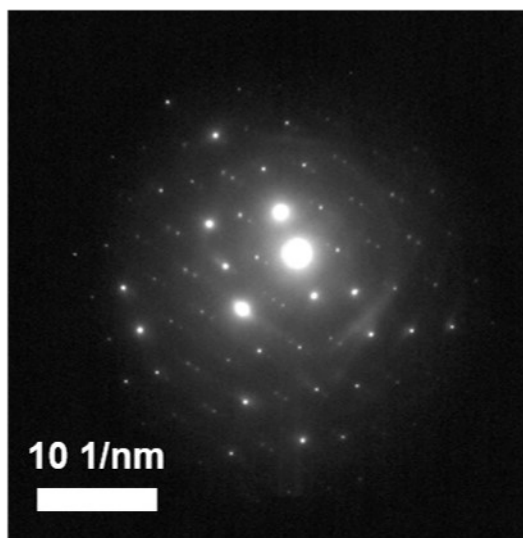
Figure S6. Specific surface area of SS-synthesis samples.



a

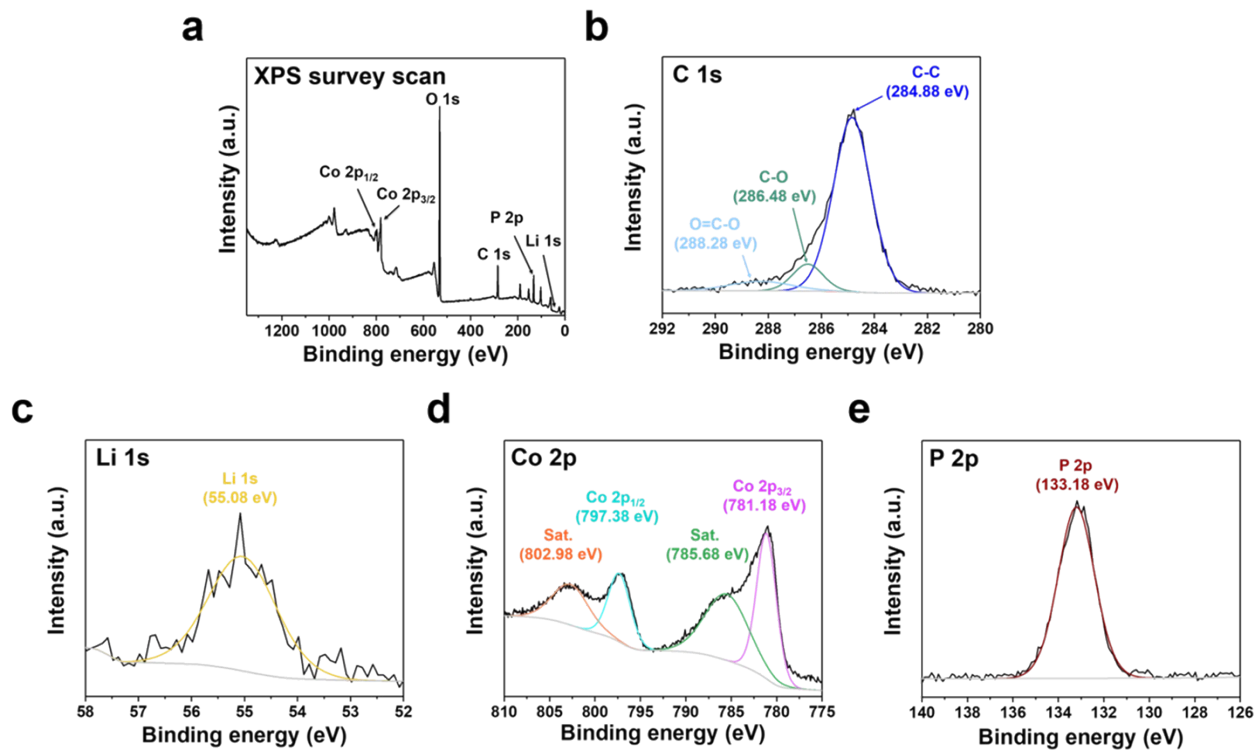


b

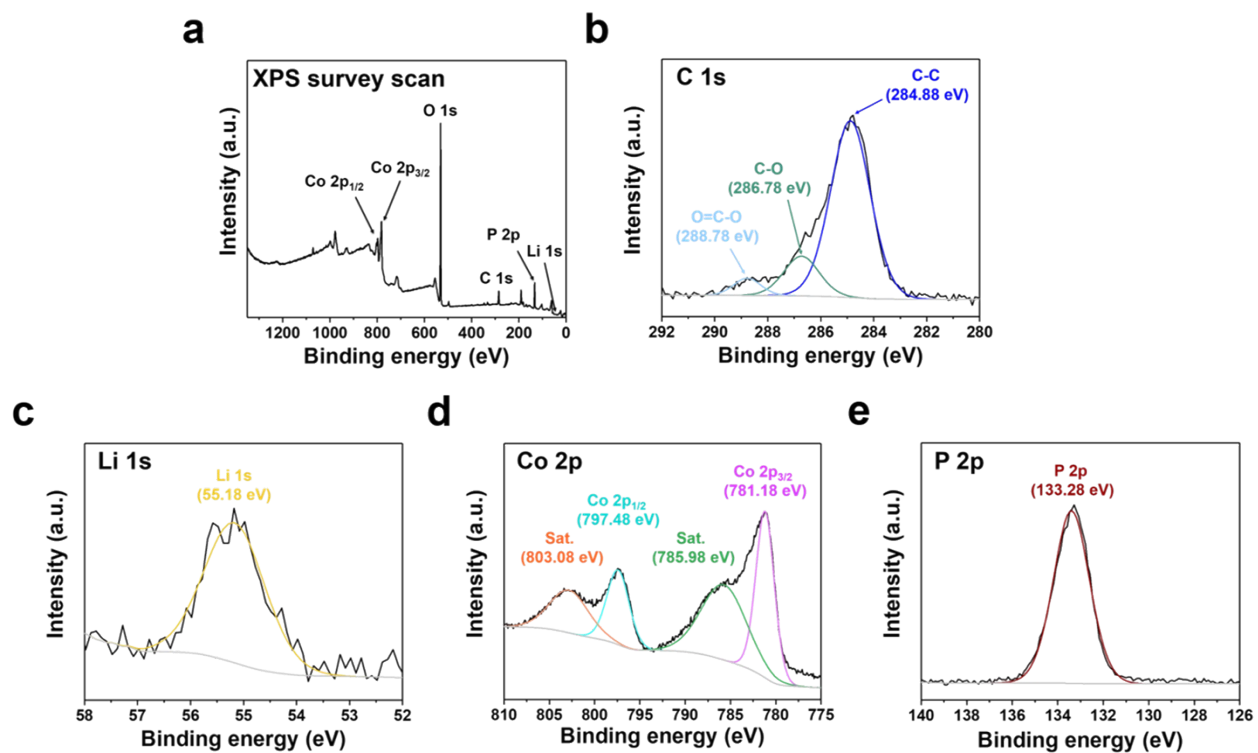


Fig

Figure S7. (a) HRTEM and (b) SAED pattern of HT-LCP.



**Figure S8. XPS spectra of HT-LCP: (a) Survey scan, (b) C 1s spectrum, (c) Li 1s spectrum, (d) Co 2p spectrum, and (e) P 2p spectrum.**



**Figure S9. XPS spectra of SS-LCP: (a) Survey scan, (b) C 1s spectrum, (c) Li 1s spectrum, (d) Co 2p spectrum, and (e) P 2p spectrum.**

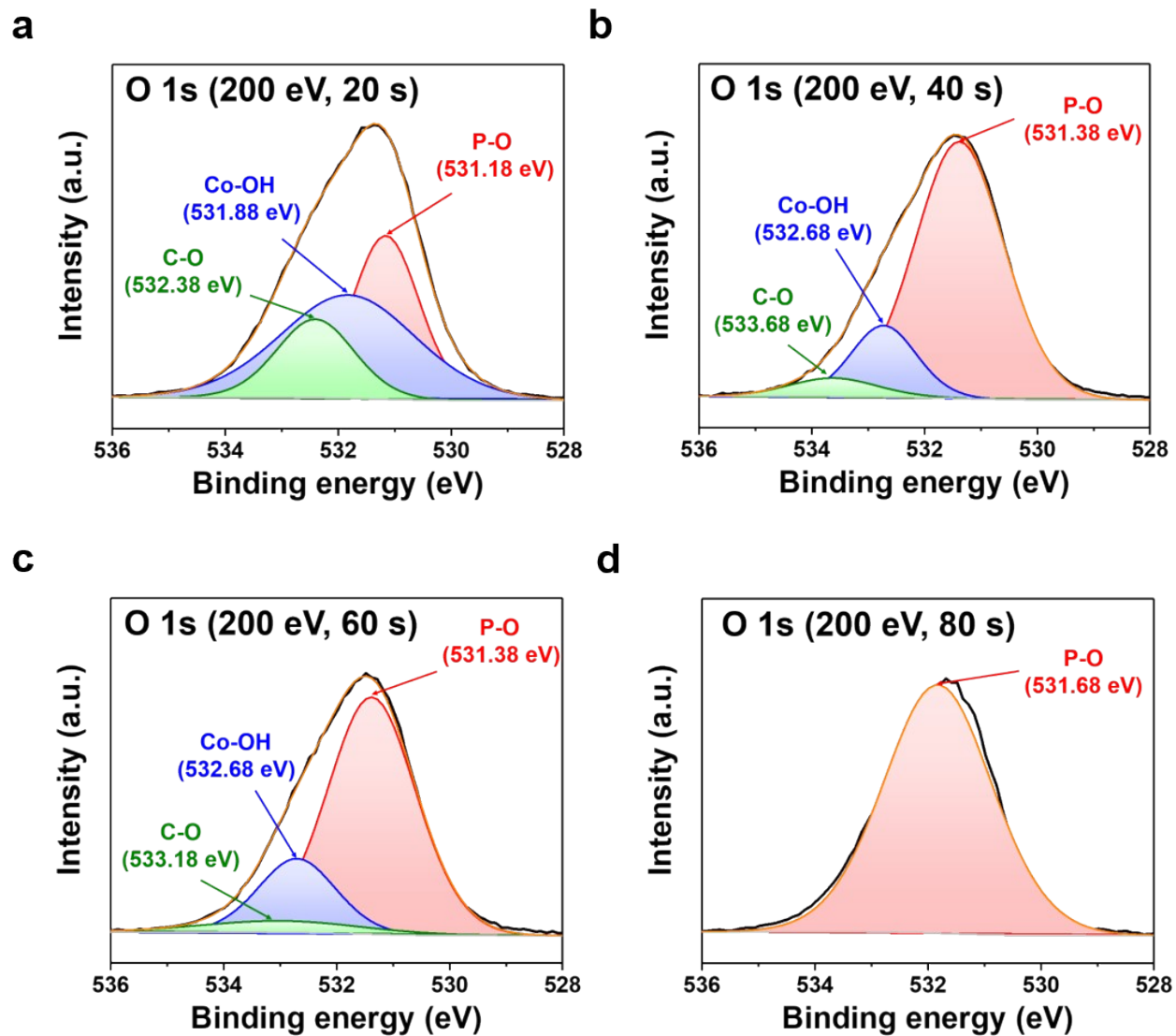


Figure S10. XPS depth profile (O 1s) of HT-LCP with 200 eV laser for (a) 20 seconds, (b) 40 seconds, (c) 60 seconds and (d) 80 seconds.

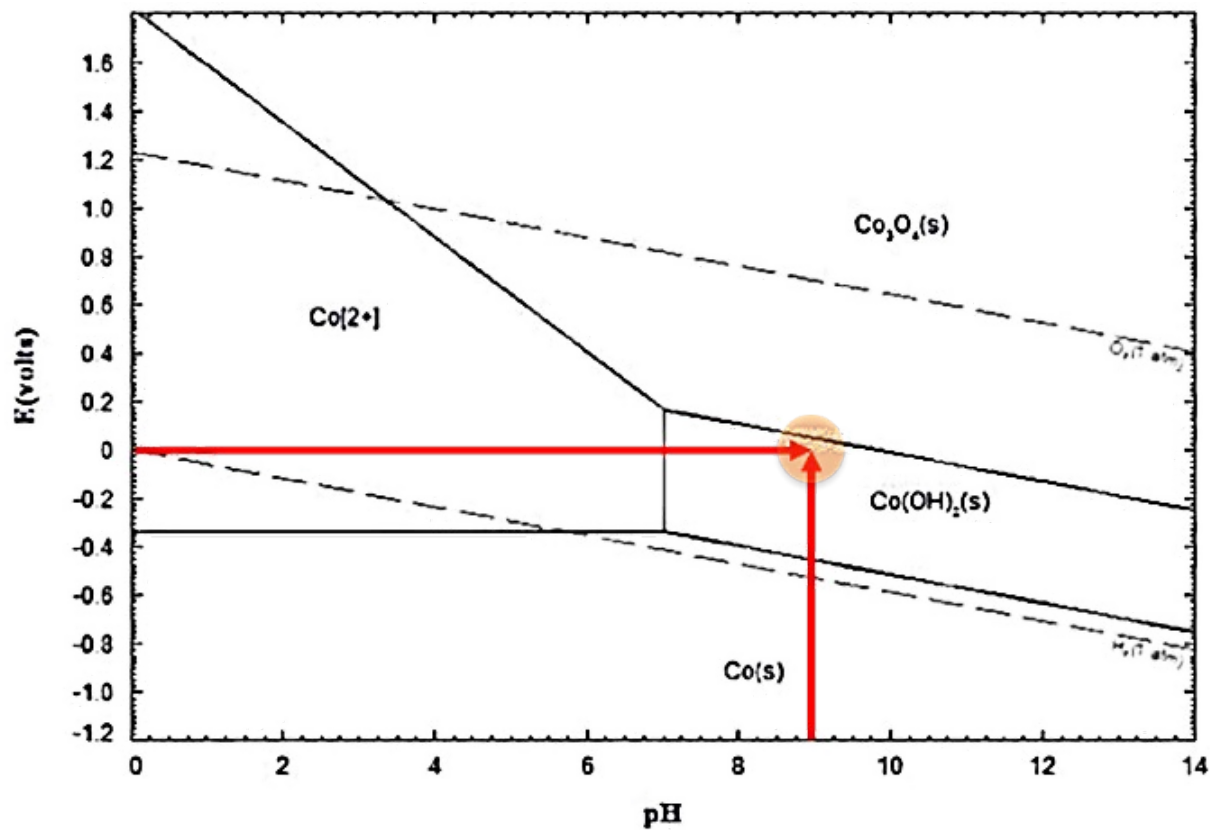


Figure S11. Pourbaix diagram of cobalt (Co-H<sub>2</sub>O at 298.15 K, 0.01 M).<sup>89</sup>

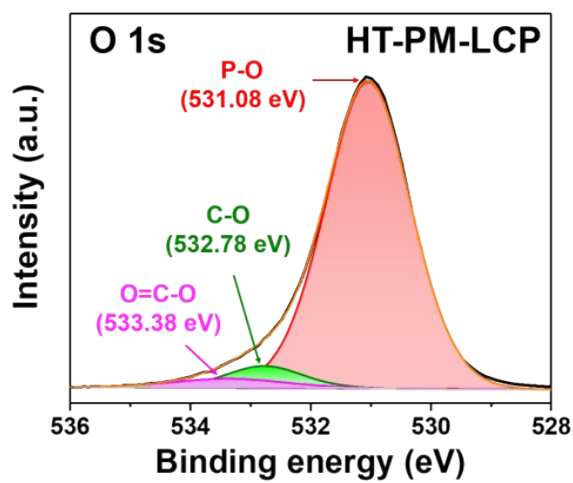
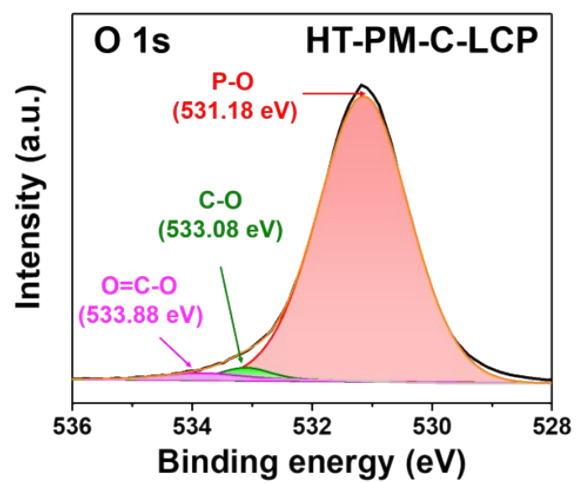
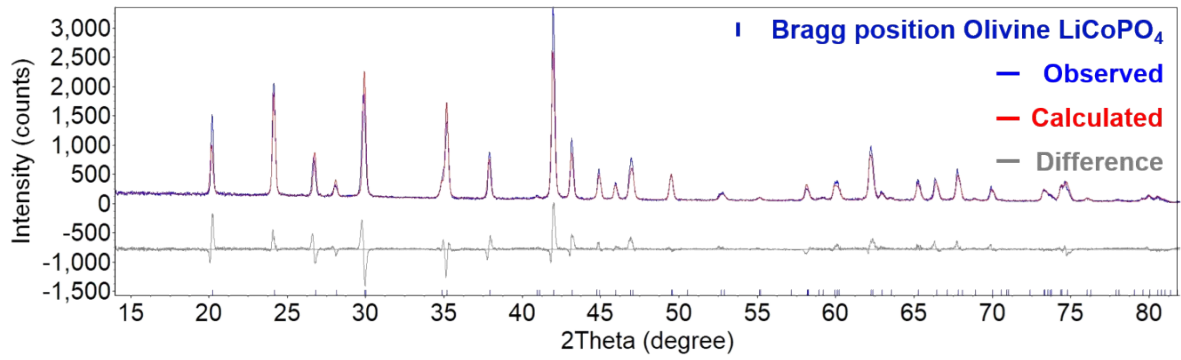
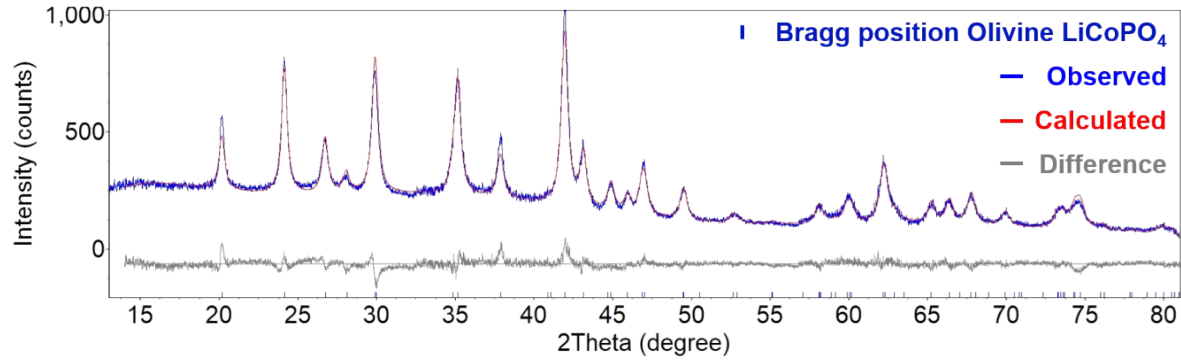
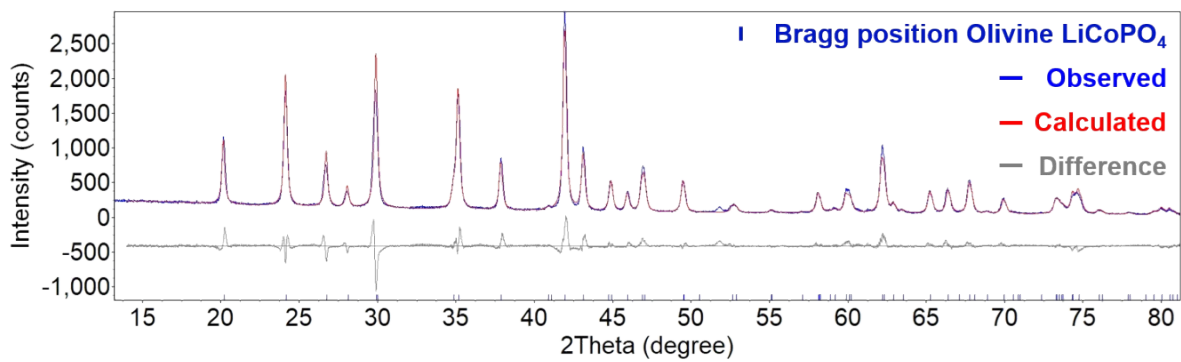
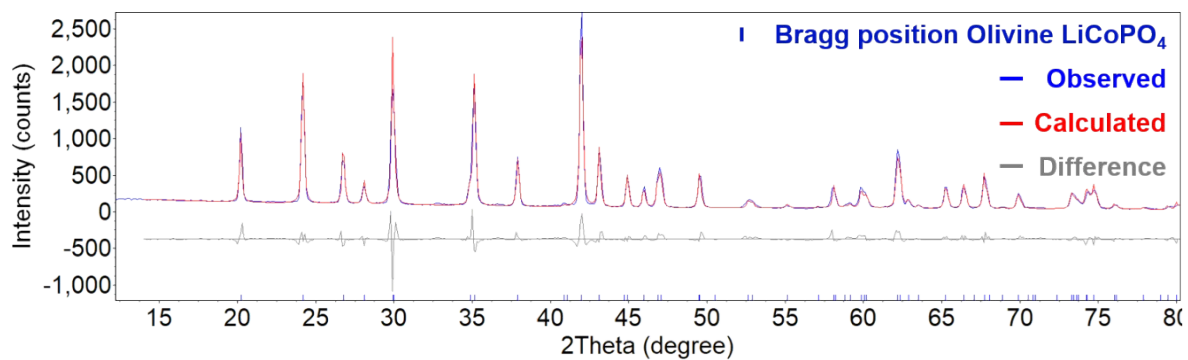
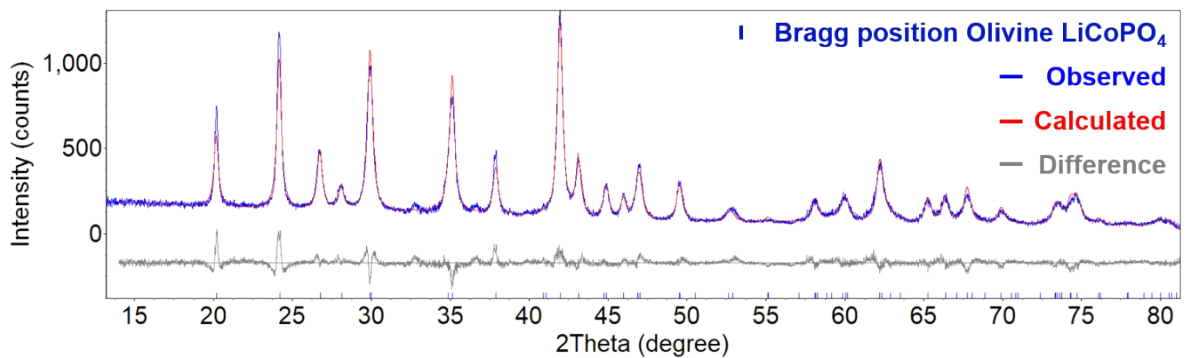
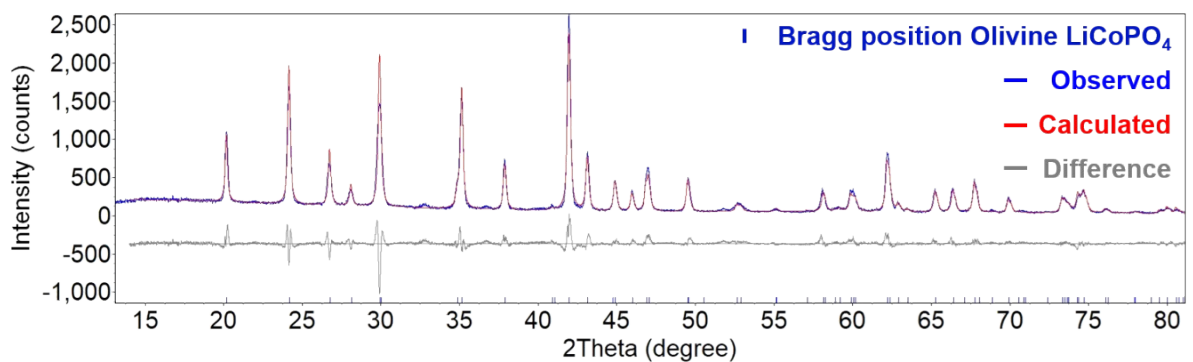
**a****b**

Figure S12. XPS O 1s spectra of (a) HT-PM-LCP, and (b) HT-PM-C-LCP.

**a****b****c**

**d****e****f**

**Figure S13. XRD Rietveld refinement of HT-LCP and SS-LCP samples: (a) HT-LCP, (b) HT-PM-LCP, (c) HT-PM-C-LCP, (d) SS-LCP, (e) SS-PM-LCP, and (f) SS-PM-C-LCP.**