

# Supporting Information

## Inserting Co and P into MoS<sub>2</sub> Photocathodes: Enhancing Hydrogen Evolution Reaction Catalytic Performance by Activating Edges and Basal Planes with Sulfur Vacancies

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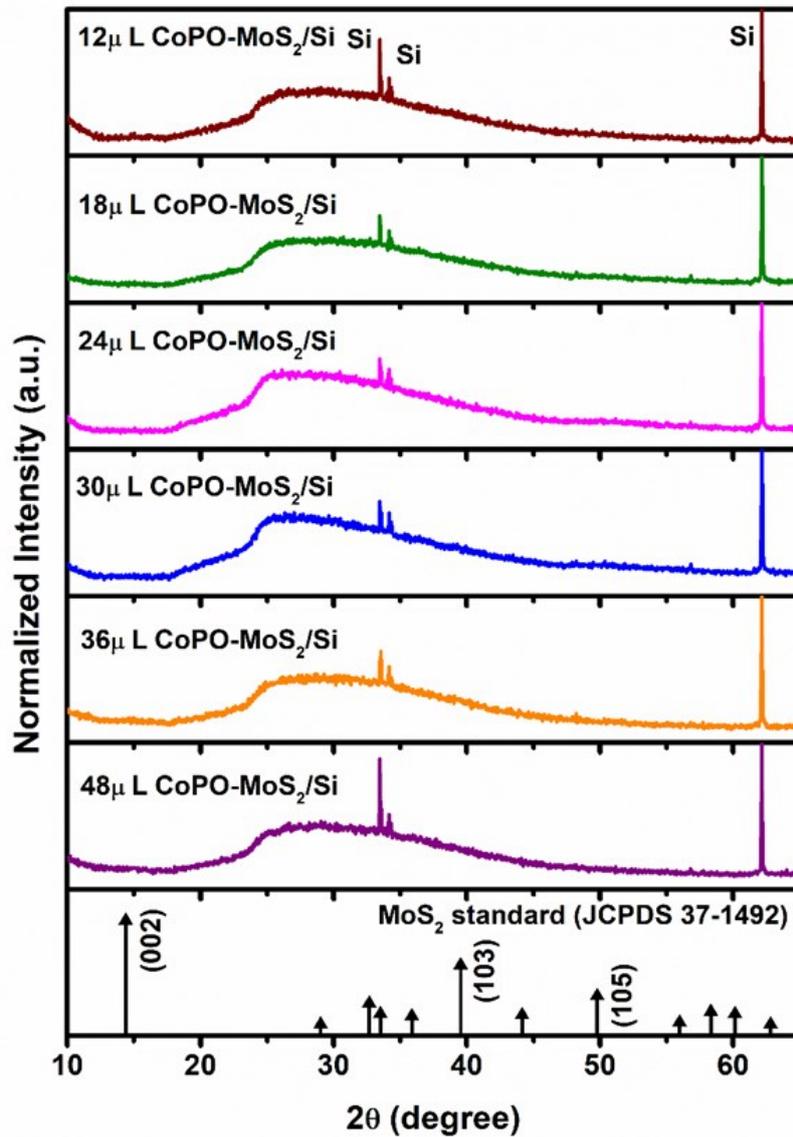
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**Figure S1.** X-ray diffraction patterns of CoPO–MoS<sub>2</sub>/Si materials after annealing after different loading of precursor solution.

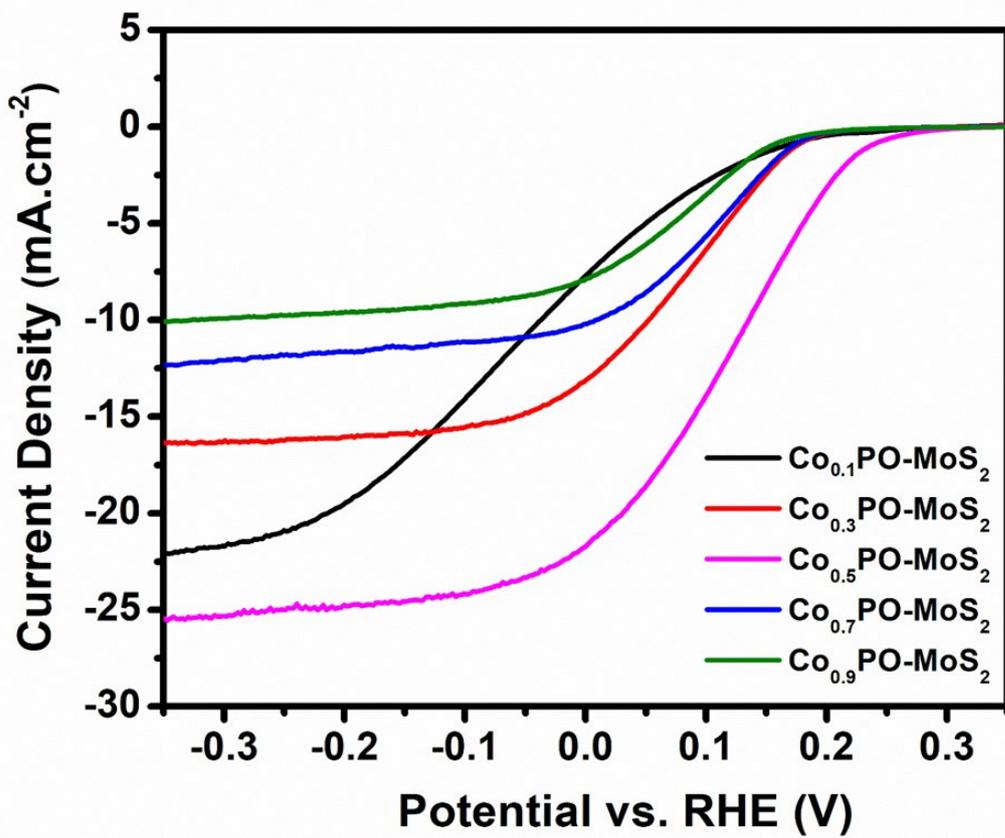
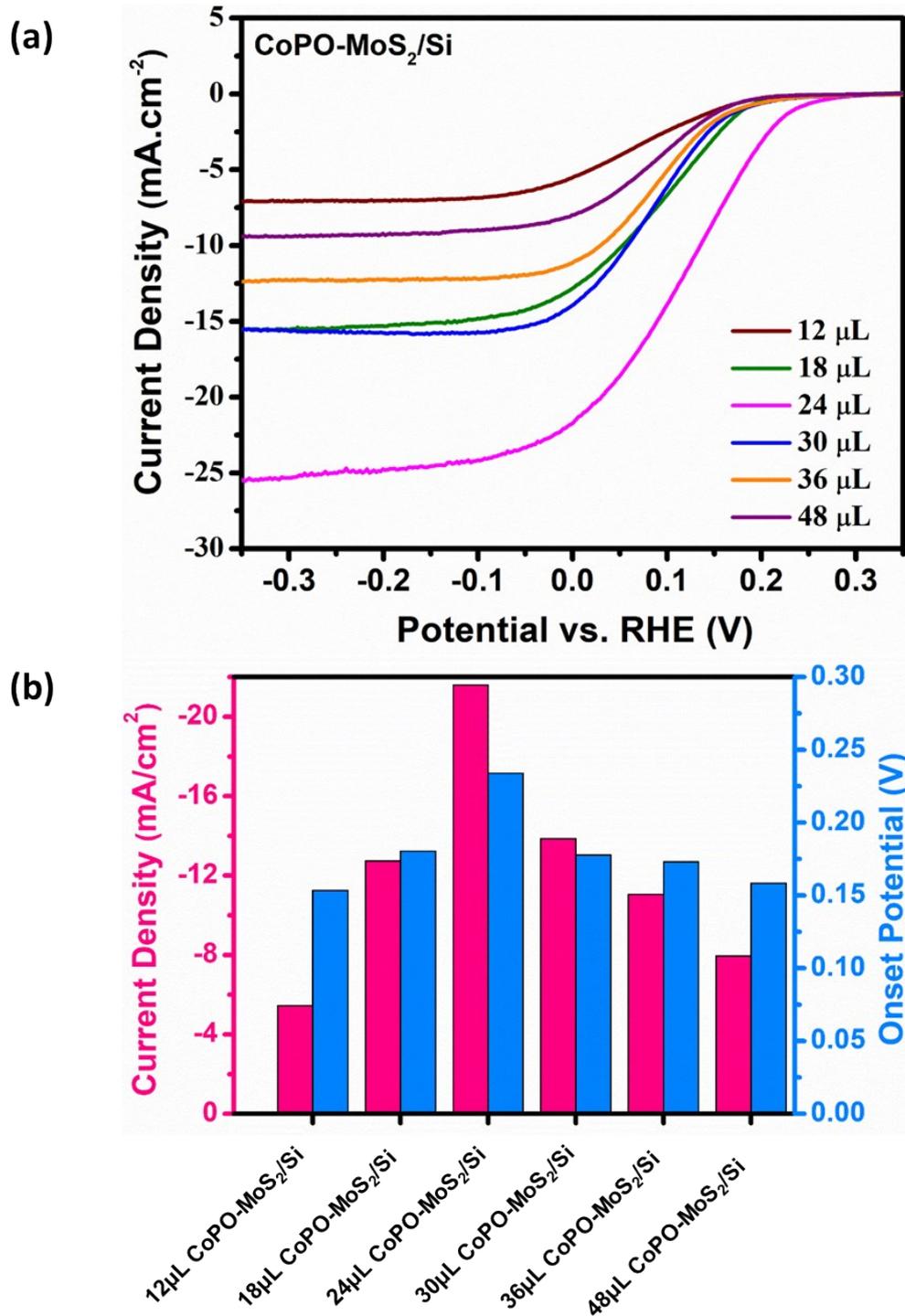
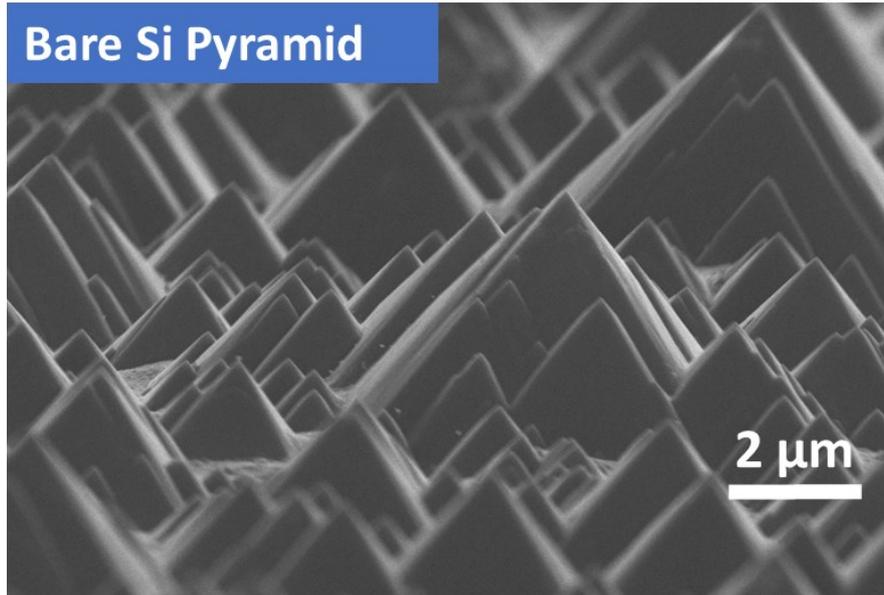


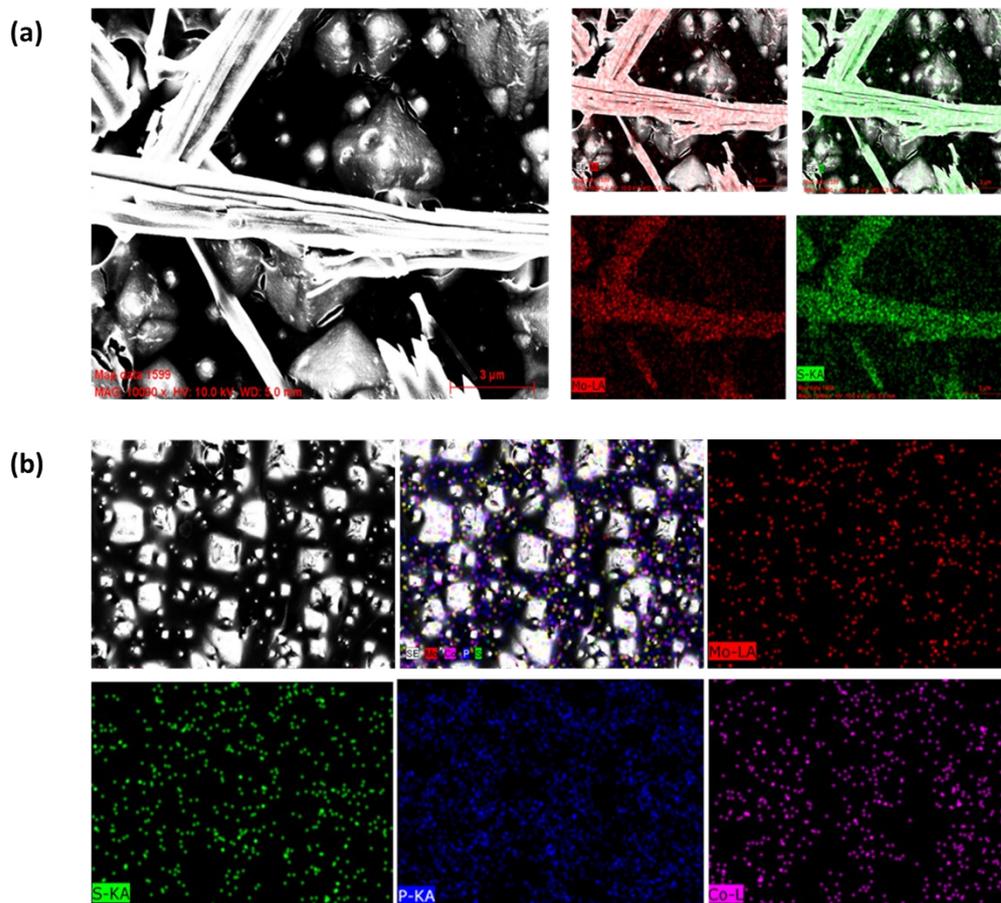
Figure S2. Linear sweep voltammograms of CoPO-MoS<sub>2</sub>/Si photocathodes using different ratio of Co under solar illumination



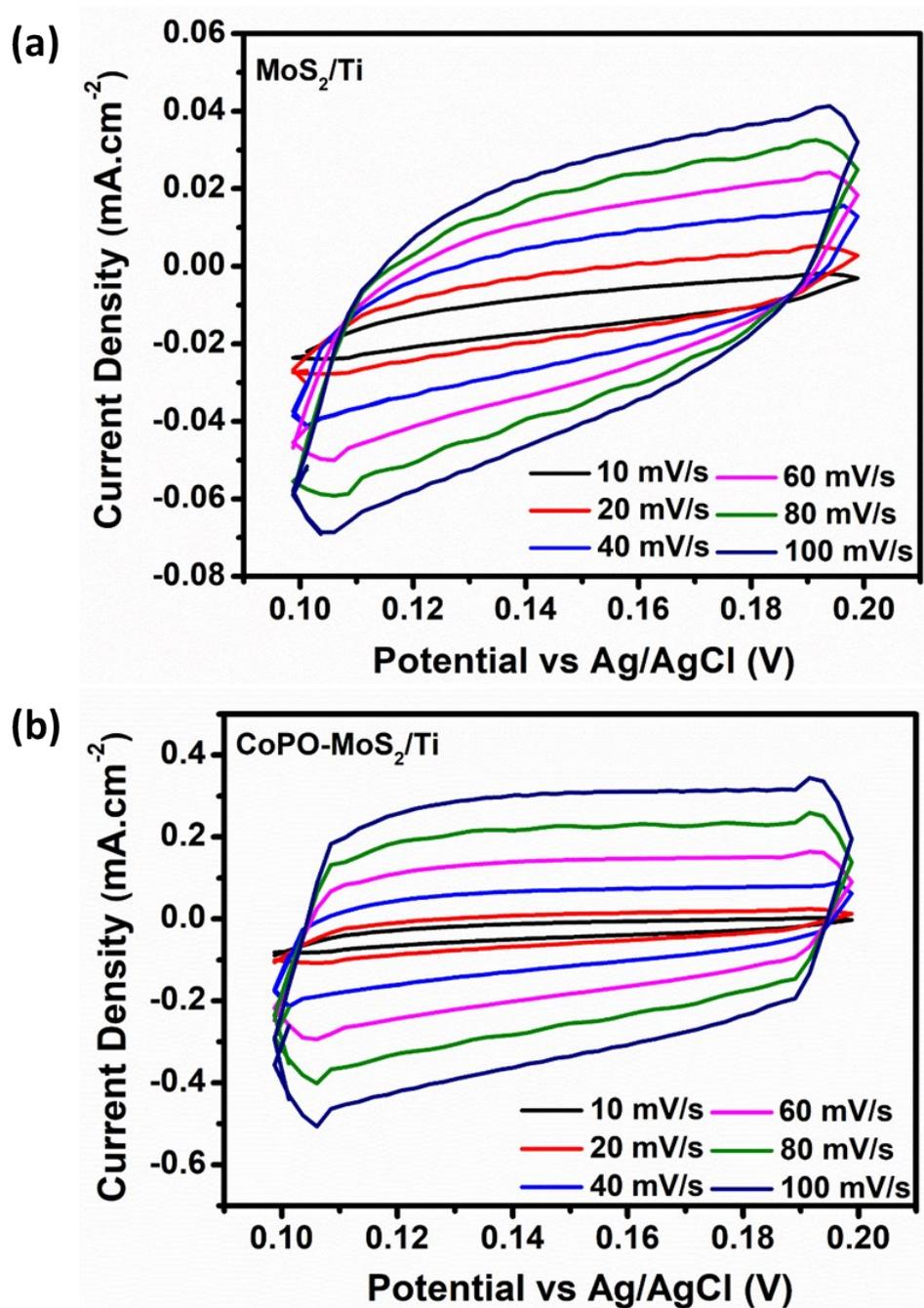
**Figure S3.** (a) Linear sweep voltammograms of CoPO-MoS<sub>2</sub>/Si photocathodes using different loading amounts under solar illumination, (b) Current density at 0 V (vs. RHE) and onset potential of photocathode materials.



**Figure S4.** Scanning electron microscope image of bare SiMPs arrays.



**Figure S5.** Energy dispersive X-ray spectroscopy images of (a) Bare  $\text{MoS}_2/\text{Si}$  and (b) Drop-casted  $\text{CoPO-MoS}_2/\text{Si}$  photocathodes.



**Figure S6.** Cyclic voltammograms of (a) bare MoS<sub>2</sub>/Ti and (b) CoPO-MoS<sub>2</sub>/Ti recorded between 0.1 and 0.2 V (vs. RHE) at various scan rates in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte.

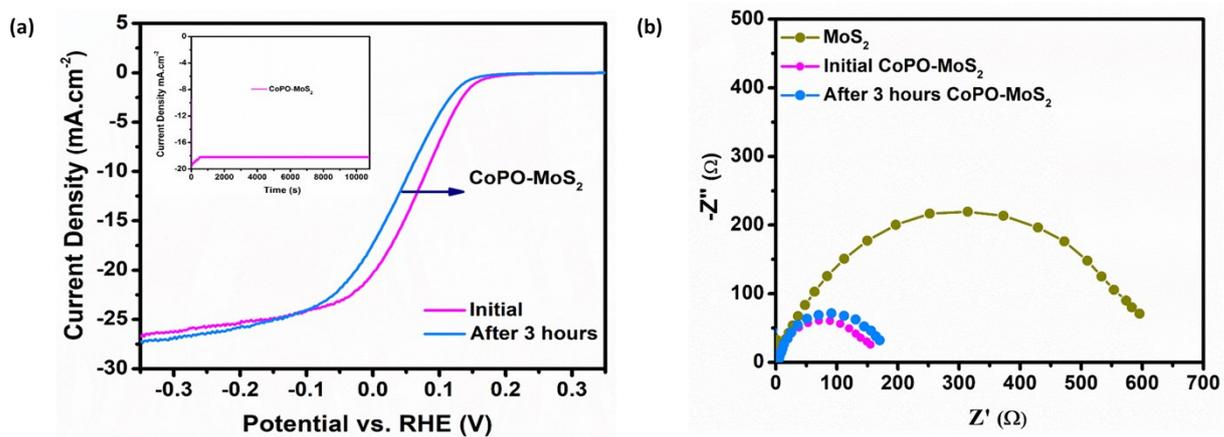


Figure S7. (a) Stability (b) Impedance for CoPO-MoS<sub>2</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte.

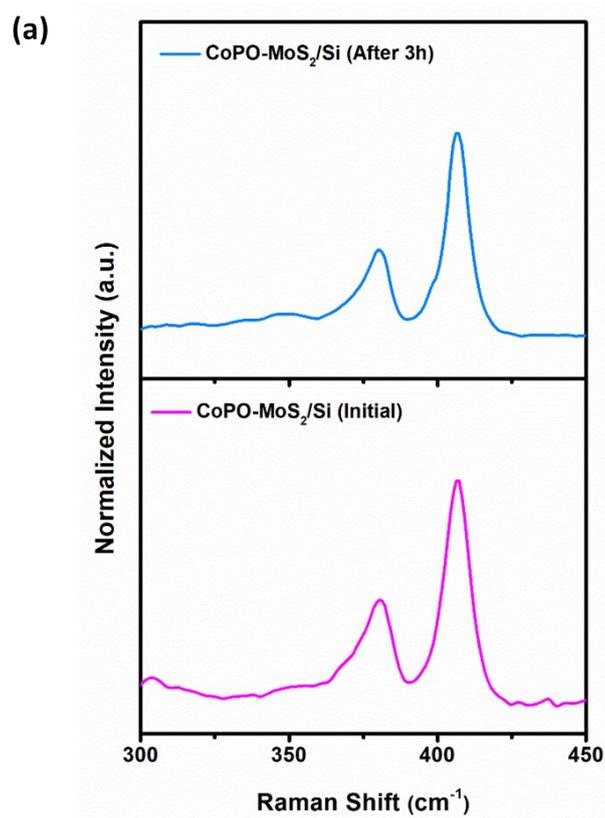
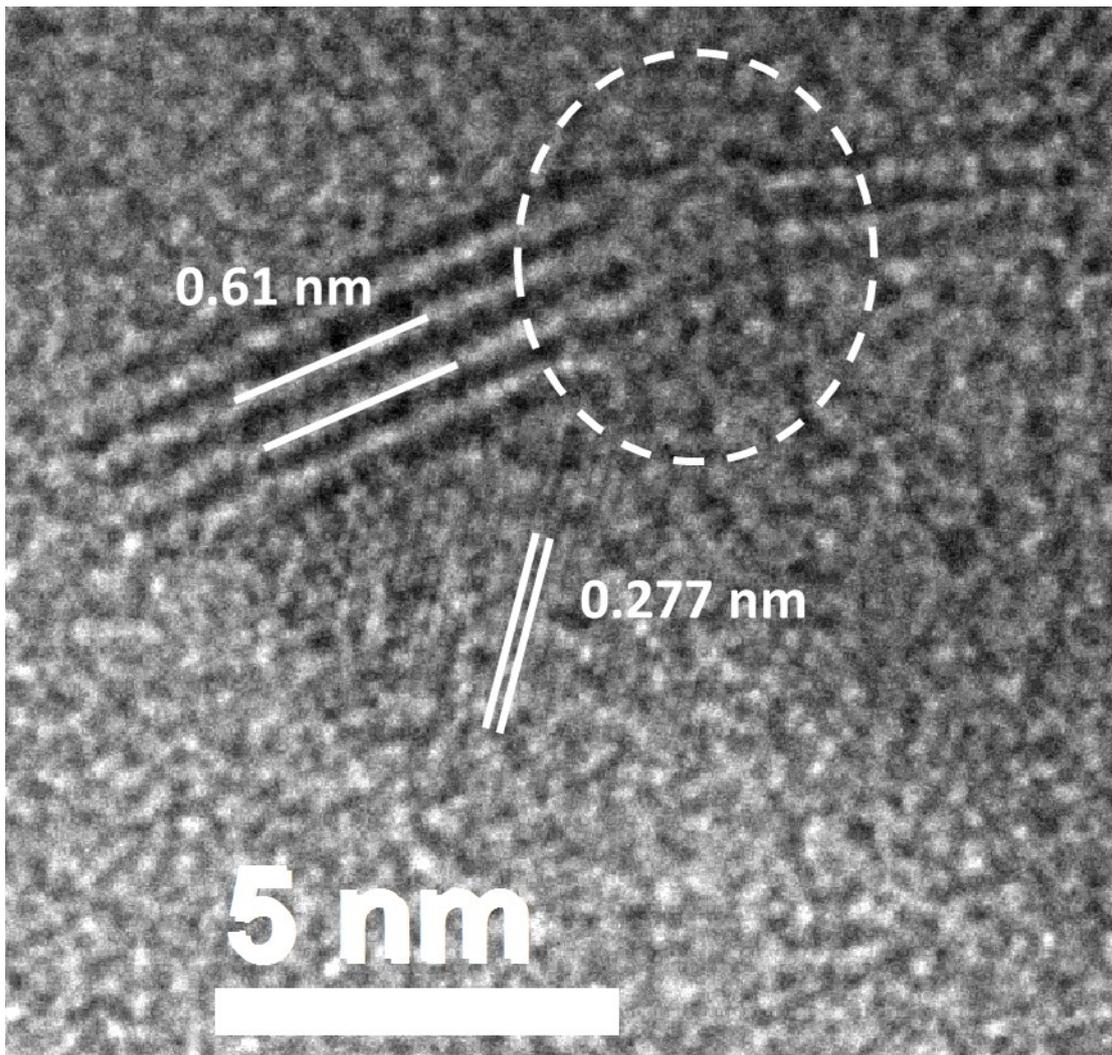


Figure S8. (a) Raman spectroscopy for initial and after 3 hours stability.



**Figure S9.** HRTEM image of CoPO-MoS<sub>2</sub> indicating presence of defects