

Supporting Information

## A crystalline and 3D periodically ordered mesoporous quaternary semiconductor for photocatalytic hydrogen generation

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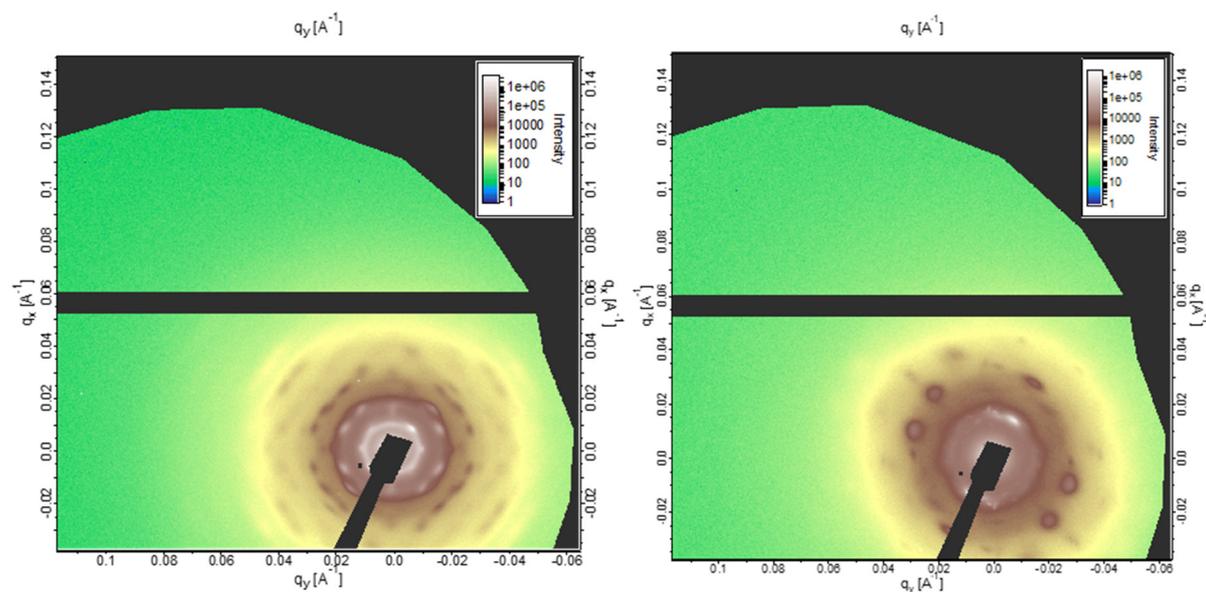
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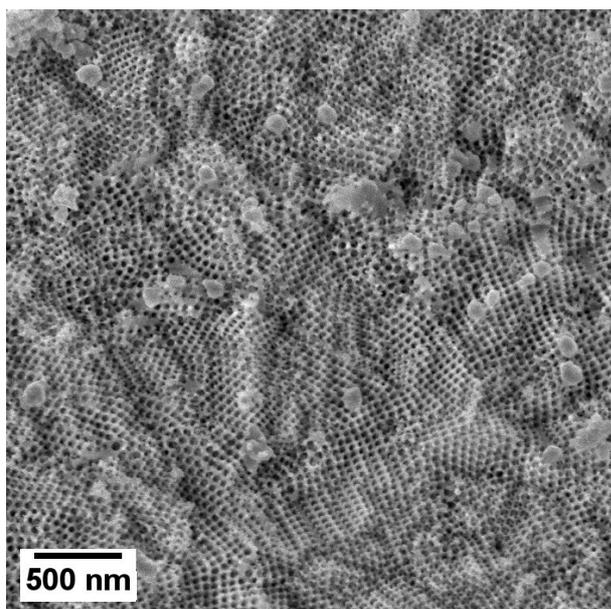
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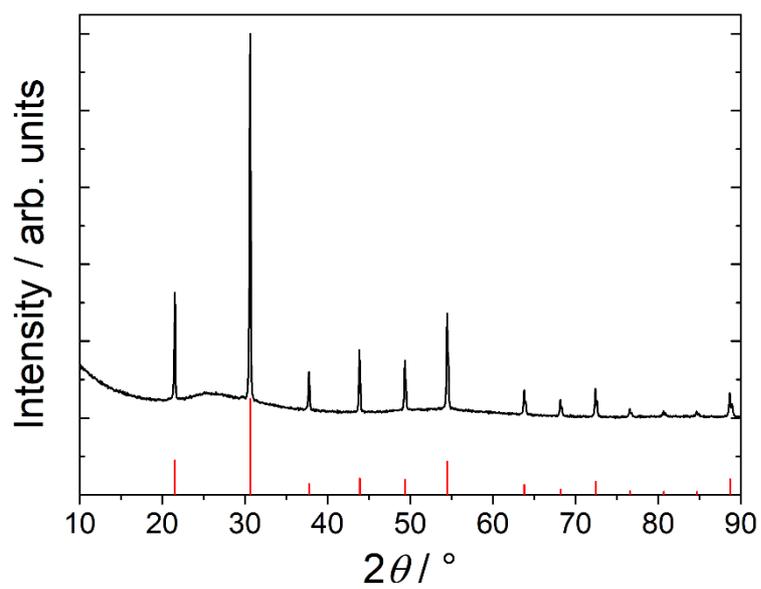
### Results and Discussion



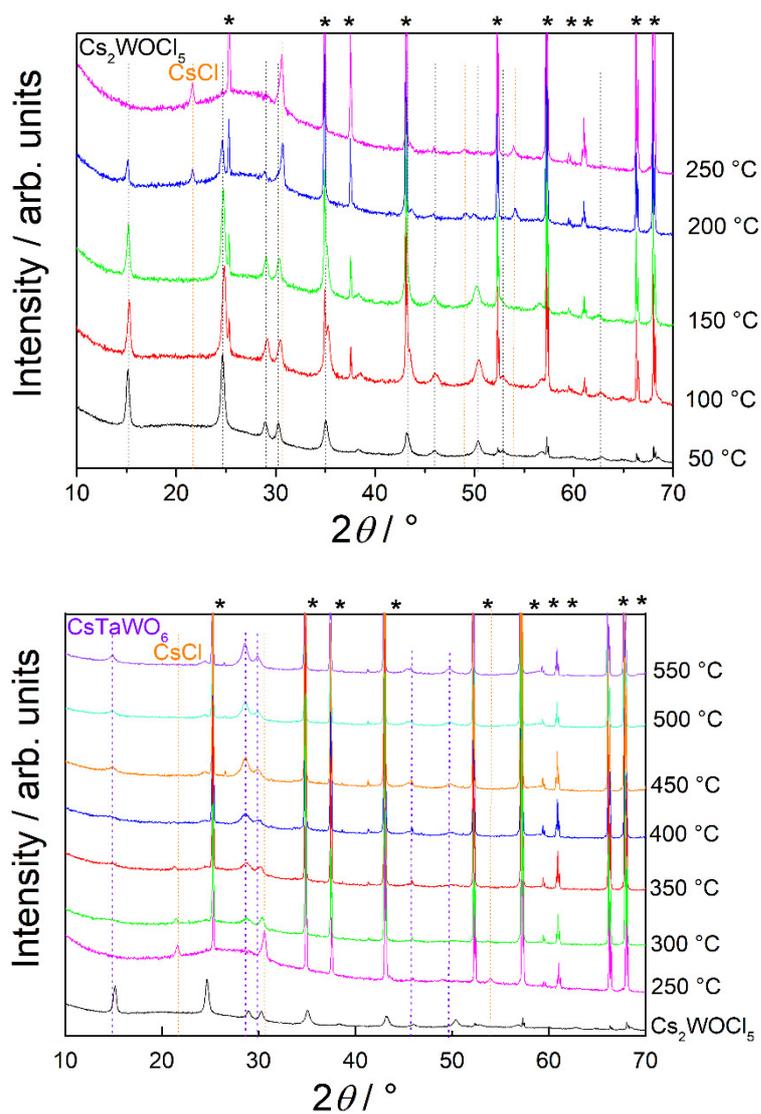
**Figure S1.** Two-dimensional SAXS datasets before (left) and after (right) calcination showing several spots indicative of orientation or large grain sizes.



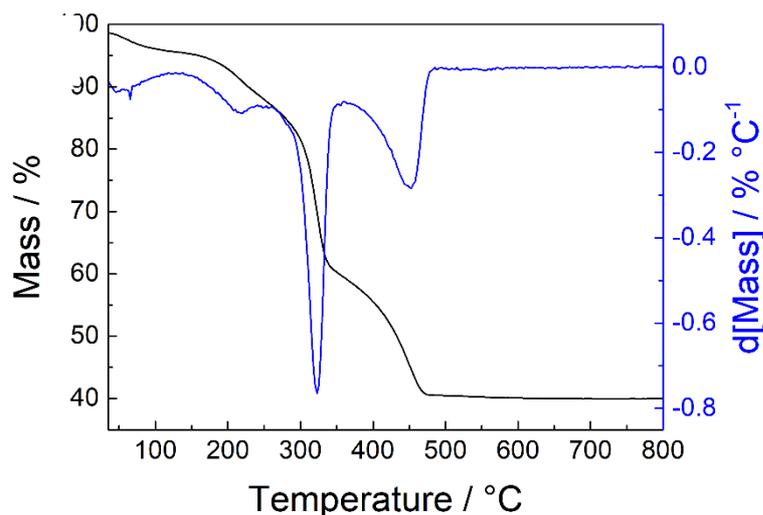
**Figure S2.** Low magnification SEM image of ISO-derived mesoporous CsTaWO<sub>6</sub>



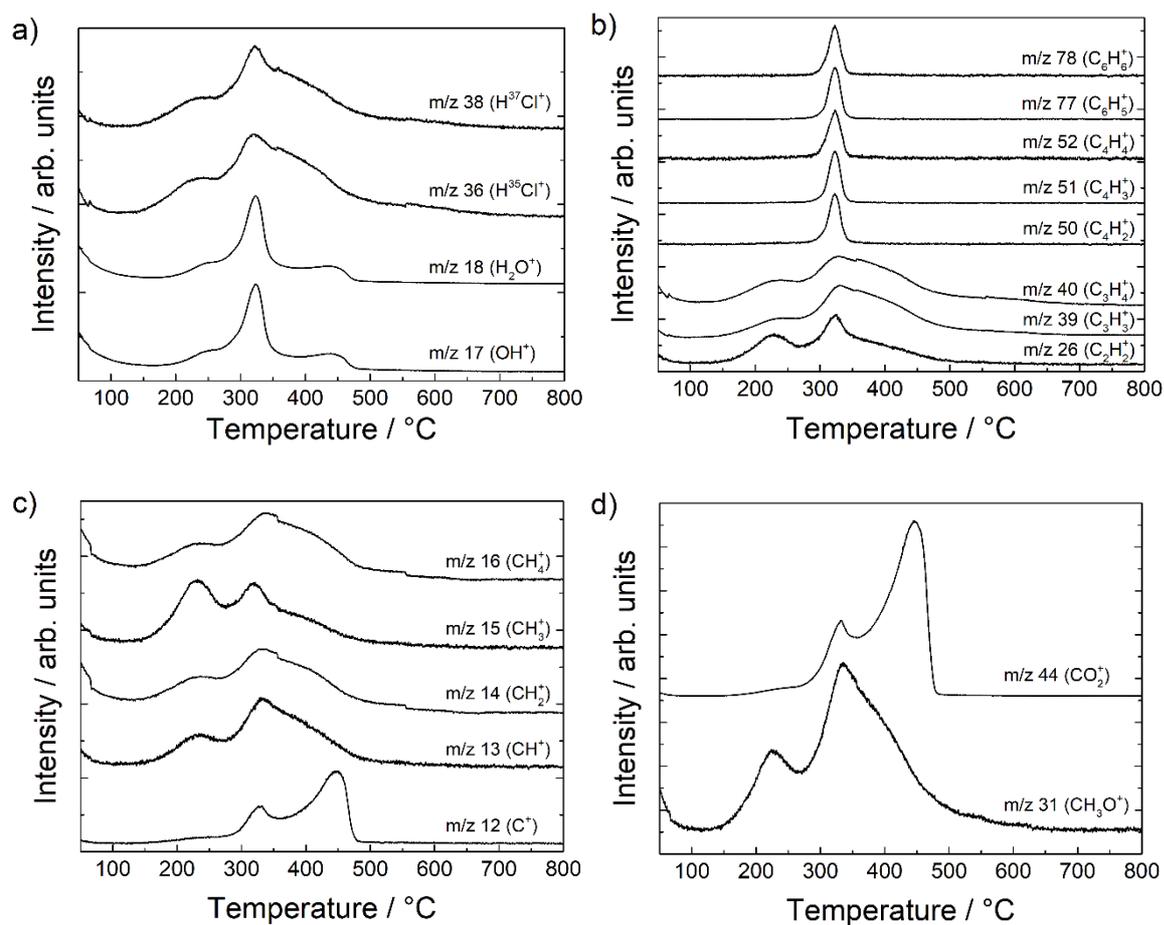
**Figure S3.** XRPD pattern of the product of Cs<sub>2</sub>CO<sub>3</sub> plus TaCl<sub>5</sub> dissolved in EtOH and dried at 80 °C. The bottom shows a reference card for CsCl (JCPDS card no. 02-2173).



**Figure S4.** *In-situ* XRPD patterns of the dried ISO- $\text{Cs}_2\text{WOCl}_5$  composite with reference lines for CsCl (orange, JCPDS card no. 02-1445) and  $\text{CsTaWO}_6$  (purple, JCPDS card no. 25-0233), calcined at different temperatures (\* assigned to reflections from the sample carrier).



**Figure S5.** TG and DTG data for ISO-derived mesoporous CsTaWO<sub>6</sub>



**Figure S6.** MS traces of ISO-derived CsTaWO<sub>6</sub>, a) water- and chlorine-derived signals; b) large bigger organic fragments from polystyrene (PS); c) smaller organic fragments from polyethylene oxide (PEO) and polyisoprene (PI); and d) other fragments, including CO<sub>2</sub>, which is released up to 500 °C.