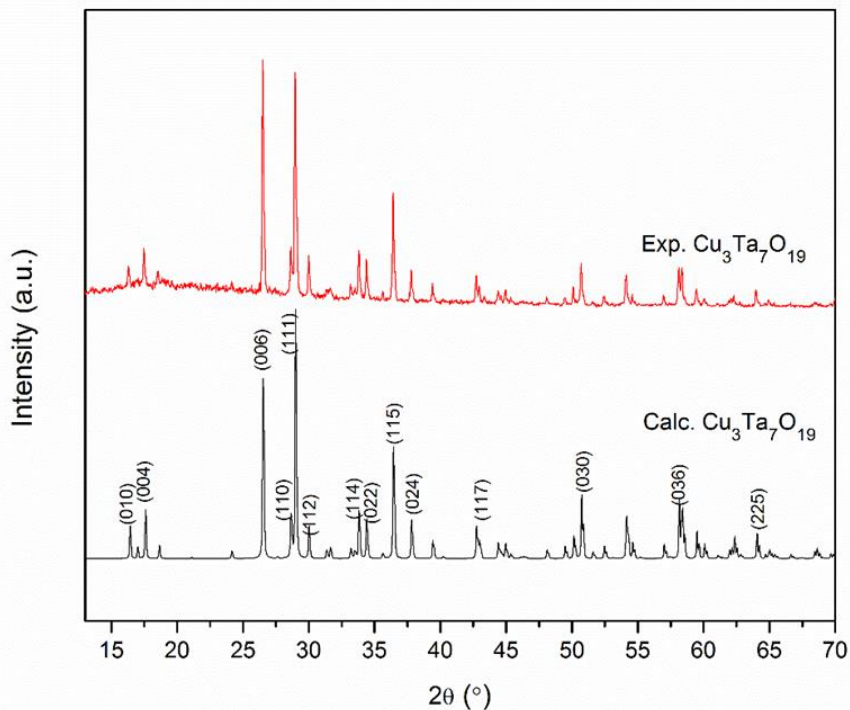


## Supporting Information

“A Metastable p-Type Semiconductor as a Defect-Tolerant Photoelectrode”

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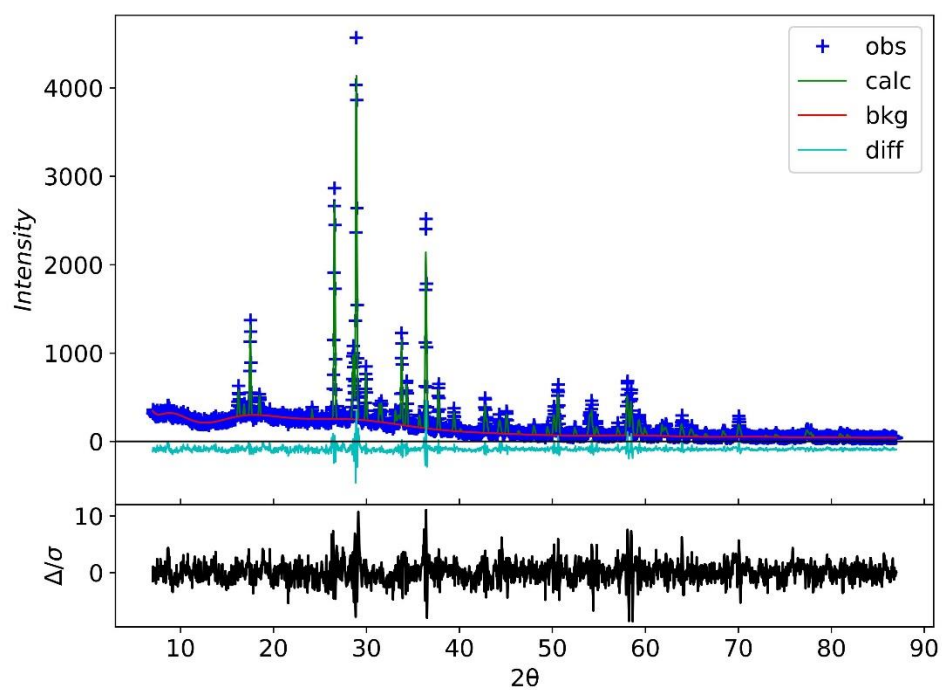
**Figure S1.** Powder X-ray diffraction pattern of the as-synthesized  $\text{Cu}_3\text{Ta}_7\text{O}_{19}$  (upper) and of the calculated theoretical pattern (lower).

**Table S1.** Selected Rietveld refinement parameters for Cu<sub>2.66(1)</sub>Ta<sub>7</sub>O<sub>19</sub>.

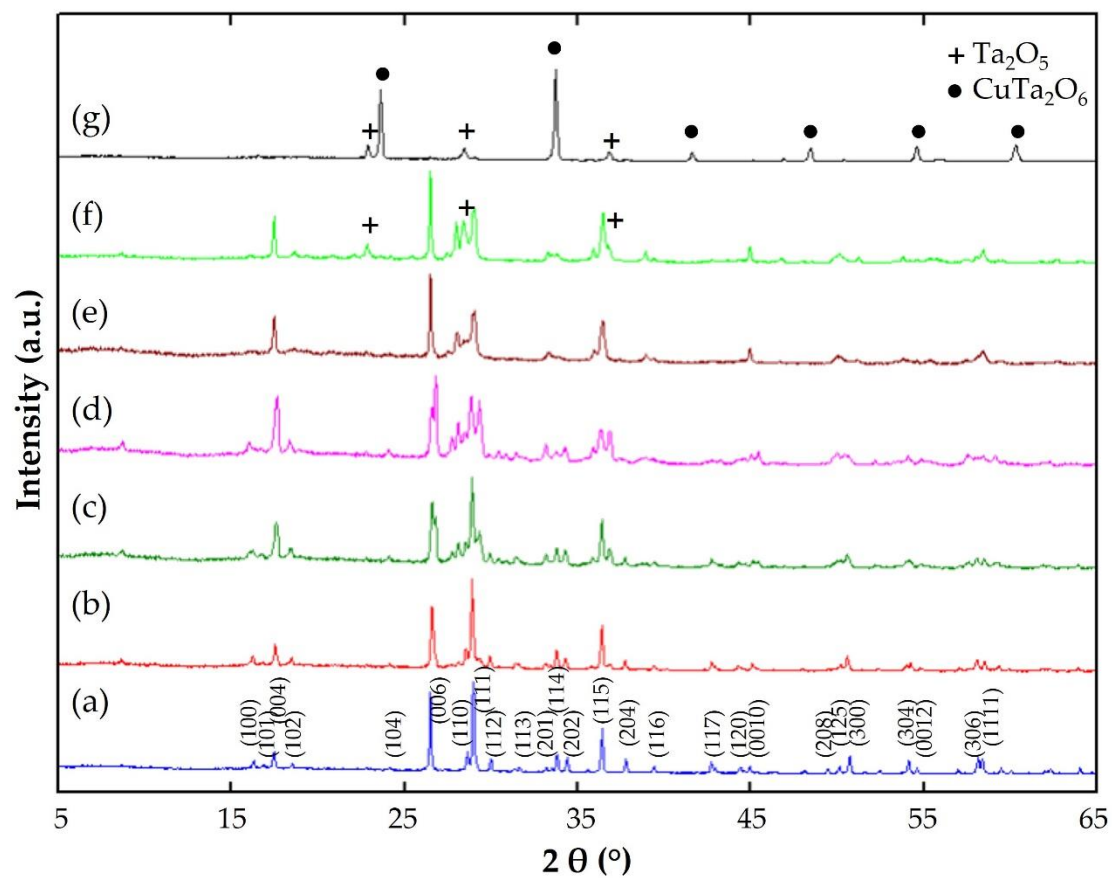
|  |   |
|--|---|
| Formula                                      | Cu <sub>2.66(1)</sub> Ta <sub>7</sub> O <sub>19</sub>                         |
| Formula weight (g/mol)                       | 1739.8  |
| Space group, Z                               | P6 <sub>3</sub> /m  |
| Radiation                                    | Cu K $\alpha$ <sub>1</sub> = 1.54051 Å<br>K $\alpha$ <sub>2</sub> = 1.54433 Å |
| Crystal system                               | Hexagonal   |
| <i>a</i> /Å                                  | 6.2403(1)   |
| <i>c</i> /Å                                  | 20.0835(3)  |
| Volume/Å <sup>3</sup>                        | 677.30(2)   |
| <i>R<sub>p</sub></i> , <i>R<sub>wp</sub></i> | 0.0561, 0.0945  |
| 2 $\theta$ (°) range                         | 10–110  |
| No. of unique data                           | 5834  |

**Table S2.** Refined unit cell dimensions and volume for Cu<sub>3</sub>Ta<sub>7</sub>O<sub>19</sub> after heating in air.

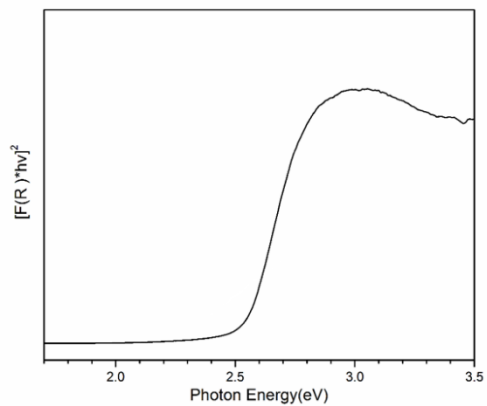
| Time (min),<br>450 °C in Air | <i>a</i> (Å) | <i>c</i> (Å) | Volume (Å <sup>3</sup> ) | $\Delta$ Volume |
|------------------------------|--------------|--------------|--------------------------|-----------------|
| 0                            | 6.226(1)     | 20.159(7)    | 676.766                  | 0               |
| 20                           | 6.253(1)     | 20.120(7)    | 681.469                  | +4.69           |
| 40                           | 6.257(2)     | 20.15(1)     | 683.360                  | +6.59           |
| 60                           | 6.261(1)     | 20.161(9)    | 684.617                  | +7.84           |
| Time (min),<br>550 °C in Air | <i>a</i> (Å) | <i>c</i> (Å) | Volume (Å <sup>3</sup> ) | $\Delta$ Volume |
| 0                            | 6.226(1)     | 20.159(7)    | 676.766                  | 0               |
| 20                           | 6.256(1)     | 20.055(6)    | 679.779                  | +3.00           |
| 40                           | 6.26(1)      | 20.13(5)     | 684.780                  | +8.00           |
| 60                           | 6.27(1)      | 20.13(6)     | 686.770                  | +9.99           |



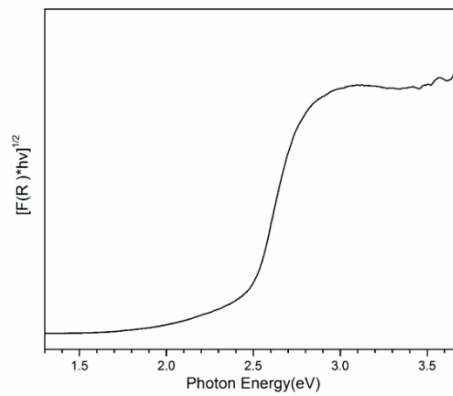
**Figure S2.** Rietveld refinement of  $\text{Cu}_{2.66(1)}\text{Ta}_7\text{O}_{19}$  after heating to 350 °C for 60 min.



**Figure S3.** Powder X-ray diffraction patterns for  $\text{Cu}_3\text{Ta}_7\text{O}_{19}$  before heating (a), and after heating in air at 400 °C for 3 h (b), 400 °C for 12 h (c), 450 °C for 12 h (d), 550 °C for 3 h (e), 650 °C for 3 h (f) and 750 °C for 3 h (g).

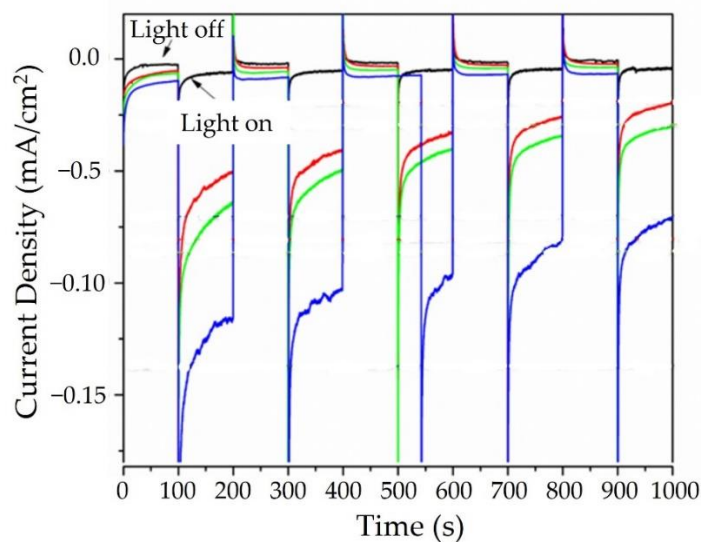


(left)

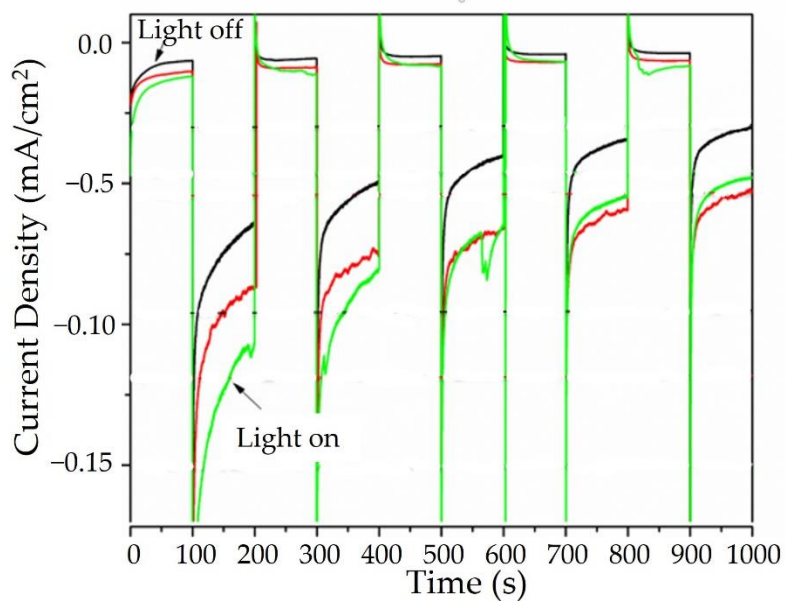


(right)

**Figure S4.** Tauc plots for  $\text{Cu}_3\text{Ta}_7\text{O}_{19}$  for the direct bandgap transition (**left**) and indirect bandgap transition (**right**).



**Figure S5.** Current density versus applied potential in an aqueous 0.5M Na<sub>2</sub>SO<sub>4</sub> solution at pH ~6.3 under chopped visible light irradiation for Cu<sub>3</sub>Ta<sub>7</sub>O<sub>19</sub> films annealed in vacuum at 500 °C, and after heating in air at 450 °C for 20 min (red), 40 min (green) and 60 min (blue).



**Figure S6.** Chronoamperometry (−0.25V applied bias) in aqueous 0.5M Na<sub>2</sub>SO<sub>4</sub> solution at pH ~6.3 under chopped visible light irradiation for Cu<sub>3</sub>Ta<sub>7</sub>O<sub>19</sub> films annealed in vacuum at 500 °C (black), and after heating in air at 450 °C for 20 min (black) 40 min (red) and 60 min (green).

**Table S3.** Refined Curie-Weiss parameters from temperature-dependent magnetic susceptibility data.

| Reaction Conditions | $\Theta$ (K) | C (emu K/mol) | TIP (emu/mol)                    | $R^2$  | $\mu_{\text{eff}}$ per Cu | %Cu(II) |
|---------------------|--------------|---------------|----------------------------------|--------|---------------------------|---------|
| None                | -3.908       | 0.0361        | $6.1 \times 10^{-5}$ (75–100 K)  | 0.9784 | 0.1790                    | 10.35   |
| 250 °C              | 8.016        | 0.0524        | $3.4 \times 10^{-4}$ (200–300 K) | 0.9612 | 0.2157                    | 12.47   |
| 350 °C              | -1.363       | 0.2298        | $8.6 \times 10^{-4}$ (65–200 K)  | 0.9993 | 0.4519                    | 26.12   |
| 450 °C              | -1.270       | 0.9468        | $3.7 \times 10^{-4}$ (50–300 K)  | 0.9996 | 0.917                     | 53.03   |