Supporting Information

CVD-grown copper tungstate thin films for solar water splitting

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Scheme S1: Synthesis of [Cu(etaoac)₂] adopted from Devi et al.¹



Scheme S2: Synthesis of [W(N^tBu)₂(dpamd)₂] according to Gwildies et al.²

Table S1: Overview of CVD parameters for stoichiometric variations of CuWO₄ thin films deposited on silicon (Si) or fluorine doped tin oxide (FTO). If not otherwise stated conditions were the same for both substrates.

Condition	Material	N_2 flow for Cu	N_2 flow for W	O ₂ flow	Time (min)	
		(sccm)	(sccm)	(sccm)		
I	CuO	25 (Si); 12.5		100	60	
		(FTO)				
II	Cu/W = 6	25	50 (Si); 100	200	60	
			(FTO)	200		
	Cu/W = 1.7	12.5	25	100	60	
			25		20	
IV	Cu/W = 1.1	12.5		100	20	
			25		20	
			25		25	
V	Cu/W = 0.4	12.5		100	10	
			25		25	
VI	WO ₃		50 (Si); 25	100	60	
			(FTO)	100	00	

In order to compensate for the affinity of the copper precursor to decompose to metallic copper and for the tungsten precursor to include nitrogen into the deposits, the vaporization temperature of the precursors was lowered to 110 °C, compared to 130 °C in previous depositions of copper films and tungsten oxynitrides. The resulting lower concentration of precursor in the gas phase and a high flow rate of oxygen were applied to allow for complete oxidation of both elements. Indeed, applying the copper precursor in oxygen atmosphere, yielded mixtures of cuprous (Cu₂O) and cupric oxide (CuO) at 400 and 500 °C, while from 600 °C onwards only crystalline cupric oxide was detected (Figure S1). The CVD of tungsten oxide by applying [W(NtBu)₂(dpamd)₂] did not give any films below 500 °C and amorphous deposits at 500 °C. At 600 and 700 °C crystalline tungsten oxide (WO₃) was observed, whereas at 800 °C a mixture of WO₃ and most possibly oxygen deficient tungsten oxides such as $W_{24}O_{68}$, $W_{18}O_{49}$ or W_5O_{14} are present (Figure S2). In a first attempt to synthesize CuWO₄ via CVD, the flow rates of the binary processes were simply added (condition II, Figure S3). The obtained deposits contained the characteristic diffractions of CuWO₄. Albeit, the crystallinity and the weight gain of the deposits was very low independent of the deposition temperature. Accordingly nitrogen

and oxygen flow rates were reduced by fifty percent (Condition III). In a different approach, inspired by Gao et al.,³ CuWO₄ was grown separately by depositing the respective binary oxide in the order 20 minutes WO₃, 20 minutes CuO and another 20 minutes WO₃. Due to the 30 minutes annealing subsequent to the deposition proper mixing of the binary oxides was achieved. Attempts to significantly influence the metal ratio via different carrier gas flows for the copper and tungsten precursor failed (not shown). Via sequential deposition of binary oxides in the order WO₃, CuO and WO₃ stoichiometric distribution of copper, tungsten and oxygen was achieved and also tungsten rich deposits were successfully synthesized.



Figure S1: XRD patterns of copper oxide deposited using $[Cu(etaoac)_2]$ in oxygen atmosphere at displayed temperatures on Si(100). The flow rates were set according to condition I. The reflex marked with an asterisk corresponds to the underlying silicon substrate. The references are taken from the ICSD reference database with the numbers 628612 (CuO) and 52043 (Cu₂O).



Figure S2: XRD patterns of tungsten oxide deposited using [W(N^tBu)₂(dpamd)₂] in oxygen atmosphere at displayed temperatures on Si(100). The flow rates were set according to condition VI. The reflex marked with an asterisk corresponds to the underlying silicon substrate. The reference is taken from the ICSD reference database with the number 50728.



Figure S3: X-ray diffraction patterns of $CuWO_4$ deposited on Si(100) at displayed deposition temperatures using condition II. Reference patterns taken from ICSD database: No. 628612 for CuO, No. 50728 for WO₃ and No. 24339 for CuWO₄. The asterisk denotes the diffraction of the underlying Si(100) substrate at 33°.



Figure S4: X-ray diffraction patterns of copper tungstate deposited on Si(100) at displayed deposition temperatures using condition III (a) and condition IV (b) after 60 minutes annealing at 750 °C in oxygen atmosphere. Reference patterns taken from ICSD database: No. 628612 for CuO, No. 50728 for WO₃ and No. 24339 for CuWO₄. The asterisk denotes the diffraction of the underlying Si(100) substrate at 33°.



Figure S5: Summary of diffraction patterns of CuWO₄ deposited at 600 °C on Si(100).



Figure S6: XRD pattern of photoanodes deposited under condition III – VI with a total duration of 4 hours at 600 °C on FTO. Reference patterns taken from ICSD database: No. 50728 for WO_3 and No. 24339 for CuWO₄.



Figure S7: RBS spectra of a) copper oxide and b) tungsten oxide thin films deposited at 600 °C on Si(100) according to conditions I and VI.



Figure S8A: Raman spectra of CuO, CuWO₄ and WO₃ deposited at 600 °C for 4 hours on FTO. Dash and solid lines track Raman shifts for WO₃ and CuO, respectively. Short blue lines show Raman shifts for pure CuWO₄. Asterisk indicates a peak from underlying FTO.



Figure S8B: Raman spectra of CuO, CuWO₄ and WO₃ deposited at 600 °C for 4 hours on FTO. The long vertical solid line tracks Raman shifts for CuO. Short blue lines show Raman shifts for pure CuWO₄.



Figure S9: Raman shifts of thick (ca. 500 nm) Cu/W = 1.1 material before and after etching with acetic acid. Dashed lines track Raman shifts for WO₃. Short red and blue lines show Raman shifts for pure CuWO₄. Asterisk indicates a peak from underlying FTO.

of 600 °C.						
Condition	C (at.%)	O (at.%)	Cu (at.%)	W (at.%)	Cu/W	M/O
I	3.4	48.0	48.6			1.01
II	3.1	55.0	35.9	6.0	6.0	0.76
III	1.3	59.6	24.8	14.2	1.7	0.65
IV	3.1	63.8	18.1	15.0	1.1	0.52
V	1.1	71.2	8.3	19.4	0.4	0.39
VI	7.9	70.5		21.6		0.31

Table S2: Elemental concentrations according to RBS/NRA measurements and calculated elemental ratios detected from samples deposited on Si(100) using conditions I to VI at deposition temperature of 600 °C.





1 µm







Figure S11: Photographs of the photoanodes on FTO with increasing tungsten content from left to right.



Figure S12: Photocurrent transients measured at thin electrodes of different composition under intermittent monochromatic irradiation (5 s dark / 5 s light) at 1.12 V vs. RHE.



Figure S13: Potential dependent photocurrent density plots of photoanodes (1 h deposition) with varying copper concentrations recorded under simulated solar light AM1.5 (1 sun; backside irradiation).



Figure S14: Absorption coefficient and light penetration depth of $CuWO_4$ deposited at 600 °C for 4 hours on FTO according to condition IV (Cu/W = 1.1).

The light diffusion length vs incident light energy for the thin Cu/W = 1.1 sample was estimated according to the formula: $\delta = 1/\alpha$ and $\alpha = -\ln(1-A)/d$ (formula from: Abdi et al., *J. Phys. Chem. C*, **2017**, *121* (1), 153–160), where δ is a light penetration depth, α is an absorption coefficient, and A and *d* stands for absorptance and layer thickness, respectively. At the maximal incident light energy used for IPCE (330 nm), the light penetration depth is ca. 100 nm. At lower excitation energies, the light penetration depth increases and reaches ca. 1400 nm at the bandgap energy.



Figure S15: Wavelength dependent current density plots of 4 hour (600 °C) deposited photoanodes of a) condition III, b) condition IV, c) condition V, and d) condition VI deposits under frontside and backside illumination. The measurements were performed in borate electrolyte (pH 7) at 1.12 V vs. RHE.



Figure S16: IPCE values of CVD deposited WO_3 with deposition times of 1 hour (solid marker) and 4 hours (open marker) on FTO substrates under backside (red) and frontside (black) illumination. The measurements were performed in borate electrolyte (pH 7) at 1.12 V vs. RHE.



Figure S17: IPCE plots under frontside irradiation for thick $CuWO_4$ (condition IV, 600 °C, 4 hour) photoanode etched with acetic acid. IPCE of thin $CuWO_4$ photoanode is also presented for comparison. The measurements were performed in borate electrolyte (pH 7) at 1.12 V vs. RHE.

Theoretical calculations



Figure S18: Band diagram of CuWO₄ according to the HSE functional. The k-points are written as explicit vectors and were taken from the evenly distributed k-mesh since many data points along high symmetry lines were difficult to converge at a reasonable computational time for the HSE functional.

E _{tot} (LDA+U) = -199.413 eV	'; E _{tot} (HSE) = -220.470 eV					
pure CuWO ₄ (2x1x1) AFM						
1.00000000000000						
9.1187050812721573	9.1187050812721573 1.0342948811336417			-0.3695901659933211		
-0.0726173182446906	0.0726173182446906 5.7403580283035591		-0.19085	5142696	6127	
0.0196485317578104	196485317578104 -0.0175092338164195		4.8386612085146377			
O Cu W						
16 4 4						
Selective dynamics						
Direct						
0.1286869286248349	0.3578272390371912	0.4284874399386682	Т	Т	Т	
0.3669236820815409	0.3829838683875260	0.0930841934706979	Т	Т	Т	
0.3887804211636753	0.9074890765729555	0.0603914991474756	Т	Т	Т	
0.1092685270896351	0.8803854503603166	0.4259354666571485	Т	Т	Т	
0.3713128838609915	0.6421728064119825	0.5715125625742147	Т	Т	Т	
0.1330763684916810	0.6170163221322357	0.9069158109313862	Т	Т	Т	
0.1112196448489992	0.0925112306728727	0.9396085291712234	Т	Т	Т	
0.3907315694140696	0.1196146342907497	0.5740646510997531	Т	Т	Т	
0.6286870558225273	0.3578271295279444	0.4284874037651341	Т	Т	Т	

0.8669236446905696	0.3829838107417439	0.0930843798151610	Т	Т	Т
0.8887803833337533	0.9074888473153125	0.0603914402245243	Т	Т	Т
0.6092683851941656	0.8803855073135541	0.4259355097543068	Т	Т	Т
0.8713130348871565	0.6421727556416486	0.5715125463221793	Т	Т	Т
0.6330763260701696	0.6170161050664973	0.9069156668632945	Т	Т	Т
0.6112196399445441	0.0925110067962344	0.9396084899618582	Т	Т	Т
0.8907315527463308	0.1196143559936503	0.5740645118610480	Т	Т	Т
0.2482531971586528	0.6558318146188957	0.2463980867618104	Т	Т	Т
0.2517468063464994	0.3441682992301305	0.7536017411650184	Т	Т	Т
0.7482529946958326	0.6558320959096926	0.2463983676042413	Т	Т	Т
0.7517469825813303	0.3441677286798041	0.7536017850526534	Т	Т	Т
0.0076824123010229	0.1729142644824056	0.2531208313454759	Т	Т	Т
0.4923176039304814	0.8270856022706913	0.7468791573115982	Т	Т	Т
0.5076823781805907	0.1729143405204822	0.2531208325302165	Т	Т	Т
0.9923175765409455	0.8270857080254826	0.7468790966709192	Т	Т	Т

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