## Supporting Information

# Unlocking the potential of semi-transparent Ta<sub>3</sub>N<sub>5</sub> photoelectrodes for high performing and reproducible solar redox flow cells

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	Type of structure	Host nanomorph ology	Ta <sub>3</sub> N <sub>5</sub> fabrication method	Dopant/ Treatment	PEC conditions (AM 1.5 G - 100 mW·cm <sup>-2</sup> )	Onset potential / V <sub>RHE</sub>	Photocurrent density at 1.23 V <sub>RHE</sub> / mA·cm <sup>-2</sup>	Year Ref.
	Planar film	None	EPD	None/Necking treatment	0.1 M Na <sub>2</sub> SO <sub>4</sub>	0.6	<i>ca</i> . 0.3 (no co-	2011
				with TaCl5 and annealing			catalyst)	1
				under NH <sub>3</sub> at 773 K for				
				30 min followed by IrO <sub>2</sub>			ca. 2.0 (with	
				co-catalyst treatment			IrO <sub>2</sub> co-catalyst	
							loading)	
	Planar film	None	EPD	None/Necking treatment	1 M NaOH	0.8	<i>ca</i> . 0.9 (no	2012
				with TaCl5 and annealing			catalyst)	2
u				under NH <sub>3</sub> at 773 K for				
Water oxidatio				30 min followed by $Co_3O_4$			ca. 2.5 (with	
				WOCs deposition			Co <sub>3</sub> O <sub>4</sub> catalyst)	
	Planar film	None	EPD	None/Necking treatment	1 M NaOH	0.9	<i>ca</i> . 1.5 (no	2016
				with TaCl5 and annealing			treatments)	3
				under NH <sub>3</sub> at 873 K for				
				60 min, followed by Co-Pi			ca. 6.1 (with Co-	
				treatment			Pi treatment)	
	Planar film	None	ALD	Ta-doped TiO <sub>2</sub> /Annealing	0.5 M K <sub>2</sub> HPO <sub>4</sub>	0.8	-	2016
				under NH <sub>3</sub> at 1023 K for				4
				30 min followed by Co-Pi			ca. 0.77 (with	
				co-catalyst treatment			Co-Pi co-	
							catalyst)	

## 1. $Ta_3N_5$ semi-transparent photoelectrodes - state of the art

Table S1: Current state-of-the-art of semitransparent  $Ta_3N_5$  photoelectrodes.

	Ta <sub>3</sub> N <sub>5</sub> Nanorods	None	EPD	Mg-doped/Necking treatment with TaCl <sub>5</sub> and annealing under NH <sub>3</sub> at 743 K for 30 min followed	1 M NaOH	0.6	<i>ca.</i> 0.8 (no doping and treatments)	2017 5
				by CoOOH treatment			<i>ca.</i> 6.5 (with Mg doping and CoOOH catalyst)	
	TaON/Ta <sub>3</sub> N <sub>5</sub> heterojunction	None	EPD	None/Necking treatment with TaCl <sub>5</sub> and annealing under NH <sub>3</sub> at 693 K for	1 M NaOH	0.35	<i>ca.</i> 0.6 (bare sample)	2018 6
				30 min under 500 mL $\cdot$ min <sup>-</sup> <sup>1</sup> NH <sub>3</sub>			<i>ca.</i> 1.5 (for TaON/Ta <sub>3</sub> N <sub>5</sub> heterojunction)	
tion	Ta <sub>3</sub> N <sub>5</sub> Nanorods	None	EPD	Sc-doped/Necking treatment with TaCl5 and annealing under NH3 at	1 M NaOH	0.40	<i>ca</i> . 0.6 (bare sample)	2018 7
/ater oxidat				713 K for 30 min under 500 mL · min <sup>-1</sup> NH <sub>3</sub> followed by Co(OH) <sub>x</sub> loading			<i>ca.</i> 5.0 (for Sc- doped $Ta_3N_5$ with Co(OH) <sub>x</sub> loading)	
*	Ta <sub>3</sub> N <sub>5</sub> Cuboids	None	EPD	None/Necking treatment with TaCl <sub>5</sub> and annealing under NH <sub>3</sub> at 713 K for 30 min under 500 mL·min <sup>-1</sup> NH <sub>3</sub> followed by Co catalyst species loading	1 M NaOH	0.20	<i>ca.</i> 0.3 (no catalyst) <i>ca.</i> 4.5 (with Co catalyst loading)	2018 8
	Ta <sub>3</sub> N <sub>5</sub> Nanorods	None	Magnetron Sputtering	None/Annealing at 1273 K under ammonia atmosphere	1 М КОН	0.6	<i>ca.</i> 0.085 (bare sample without	2023 9

S3

			with glancing angle deposition	(50 sccm flowrate), followed by FeNiCoO <sub>x</sub> co-catalyst loading			interlayer nor co-catalyst) <i>ca.</i> 10.8 (Ta <sub>3</sub> N <sub>5</sub> nanorods with 150 nm of Ta <sub>3</sub> N <sub>5</sub> interlayer and FeNiCoO <sub>x</sub> co-catalyst loading)	
	Planar film	None	EPD	Cu gradient Zr co-doped Ta <sub>3</sub> N <sub>5</sub> /NiCoFe–B <sub>i</sub> co-catalyst	1 М КОН	0.47	<i>ca.</i> 2.1 (no dopants nor co-catalysts) <i>ca.</i> 8.5 (using Cu gradient Zr co- doped Ta <sub>3</sub> N <sub>5</sub> and NiCoFe–B <sub>i</sub> co-catalyst)	2024 10
idation	Planar film	None	ALD	None/None	0.1 M K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	0.25	<i>ca</i> . 2.5 (bare sample)	2019 11
Ferrocyanide ox	Planar film	None	EPD	None/Ta-doped TiO <sub>2</sub> underlayer over FTO substrates; annealed under 100 mL·min <sup>-1</sup> NH <sub>3</sub> at 698 K for 30 min	0.1 M K <sub>4</sub> [Fe(CN) <sub>6</sub> ] in 1 M KOH	0.70	<i>ca.</i> 3.8 (bare sample)	2025 [This work]

#### 2. Underlayers band-alignment and performances (comparison)

Figure S1 shows the band-alignment energy of different underlayers tested: TiO<sub>2</sub>, TaO<sub>x</sub> and Tadoped TiO<sub>2</sub> – TTO; their conduction band (CB) are positioned below than of the Ta<sub>3</sub>N<sub>5</sub> and above that of FTO layer - Figure S1a), which makes them suitable back-contact layers, as reported elsewhere.<sup>12-14</sup> In the same way, work function ( $W_F$ ) was obtained using the Kelvin-Probe method, which is a non-invasive measurement technique. The work function is defined as the minimum energy required to remove an electron from the Fermi Level to the vacuum level in one semiconductor matrial, influencing surface-related phenomena like electron transferring and conductivity. The Kelvin-Probe setup (UHVKP020, KP Technology) includes a conductive probe (a "tip") located over the sample for which the work function is to be measured; the probe is brought very close, typically within a few micrometers, to the sample surface without making contact. In this arrangement, a region of influence forms where the electric fields of the probe and sample interact, effectively creating a capacitor system, with the probe and sample acting as plates. When two conductive materials come into contact, charge redistribution occurs until reaching an equilibrium state, creating a potential difference at the interface. A small potential is applied to the probe, leading to oscillations in the sample surface charge and the phase shift and amplitude of the oscillating signal are measured to determine the potential difference between the probe and the sample surface. By comparing this measured potential difference with known values, the work function of the material can be inferred. In this case, for TiO<sub>2</sub> and TTO, work function values obtained were 5.2 eV and 5.0 eV, respectively. It means that the amount of energy required to extract an electron from bulk to the vacuum level for TTO is lower than  $TiO_2$ , reinforcing its properties as an electron transport layer. This phenomenon was also proved by J-E performances in different Ta:TiO<sub>2</sub> ratios, which are shown in Figure S1b). A set of preliminary tests varying the concentration of Ta in TiO2 structure showed different current density performances. According to literature, Ta incorporation has resulted in two simultaneously phenomena, namely substitution of Ti atoms as well as O emptiness, resulting on more free electrons available, and consequently reducing resistivity.<sup>15</sup> However, Hamann et al.<sup>4</sup> had proved that either lower or higher Ta concentration are not favorable to decrease resistivity, indicating an optimal concentration of ca. 1.6 % of Ta. In the present study, it was possible to show that 1 cycle Ta: 71 cycles TiO<sub>2</sub> ratio was the most prominent in terms of performance (photocurrent and fill factor) among the set of different ratios studied (1:50, 1:71 and 1:125).



Figure S1: a) SEM images (top surface and cross-section) of a TTO -5 nm sample covered with Ta<sub>3</sub>N<sub>5</sub>; b) Energy band alignment diagram of FTO, Ta-doped TiO<sub>2</sub> (TTO), TiO<sub>2</sub>, TaO<sub>x</sub> and Ta<sub>3</sub>N<sub>5</sub> materials (based on: <sup>12-14, 16</sup>), and TiO<sub>2</sub> and TTO work function comparison; c) *J-E* curves obtained for Ta<sub>3</sub>N<sub>5</sub> photoelectrodes with different Ta:TiO<sub>2</sub> ratios, using 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> in 1 M KOH electrolyte.

# **3. TTO deposition over FTO glass substrates assessed by** *J-E* performances

TTO -5 nm was deposited over larger FTO glass substrates (3 cm  $\times$  3.6 cm) to check reproducibility, *i.e.* if the ALD depositions were uniform over the entire substrate. After Ta<sub>3</sub>N<sub>5</sub> photoelectrode preparation, glass substrate was cut into small pieces of 3 cm  $\times$  1.2 cm, and photoelectrochemical performances were assessed – Figure S2. The FTO + Ta<sub>3</sub>N<sub>5</sub> sample is shown together with each sample curves. A large divergence was revealed among them, proving that TTO deposition had been non-uniform which corroborates with FTO + TTO – 5 nm transmittance values closest to FTO ones.



Figure S2: *J-E* curves obtained for  $Ta_3N_5$  photoelectrodes to assess the uniformity of TTO deposition over 3.6 cm × 3.0 cm FTO glass substrates, using 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> in 1 M KOH electrolyte. Samples were cut into small ones of 3 cm × 1.2 cm (lab scale): a) sample 1; b) sample 2; c) sample 3.

#### 4. FTO – TTO substrates: transmittance spectra

The thickness of the TTO layer was studied to assess its behavior on PEC performance and reproducibility intra-batch  $Ta_3N_5$  samples. Complementarily, it was assessed how the TTO thickness could compromise the passage and light absorption by  $Ta_3N_5$ . It is important to note that absorption by the glass occurs up to 300 nm, so the measurement was carried out between 300 nm and 800 nm. The spectrum shows that there is a loss in light absorption between 10 % and 15 % comparing the thickness selected as the best - 30 nm - and the lower thickness of 5 nm – Figure S3.



Figure S3: Transmittance spectra for TTO underlayer (1 cycle Ta : 71 cycles TiO<sub>2</sub>), for different thicknesses.

#### 5. Influence of oven position during annealing (XRD spectra)

For reproducibility concerns, it is important to highlight that the samples were placed over a glass holder inside an alumina tube, over which the unidirectional flow of NH<sub>3</sub> passed from the source to the outlet. The most central part of the holder – Figure S5 - would be more suitable to assess the influence on the photoelectrodes' performance during the annealing step given that is covered by the oven resistances connected to temperature controllers, but only the samples closer to NH<sub>3</sub> source registered the best performances in terms of photocurrent, having been considered for the performance optimization. Two FTO - TTO substrates were annealed at the extremities of the central zone of the furnace at 425 °C and subjected to an XRD analysis to justify this optimization criterion. XRD spectra registered different peak intensities, according to the position of the samples in the oven – Figure S4.



Figure S4: XRD spectra for FTO-TTO substrates, annealed at the extremities of the central part of the oven ( $NH_3$  inlet and the  $NH_3$  outlet).

### 6. Optimization conditions

Table S2 shows the main conditions used to optimize the synthesis of  $Ta_3N_5$  photoelectrodes prepared by electrophoretic deposition, using a TTO underlayer as a back-contact;  $TaO_x:TiO_2$ ratio was fixed at 1:71 and a thickness of 30 nm was also adopted. After some preliminary tests, it was concluded that time of deposition, annealing temperatures and NH<sub>3</sub> flows were the factors influencing the most the match between current density and photopotential, *i.e.* the power density of  $Ta_3N_5$  photoelectrodes.

Optimization tests	Times of deposition (min)	Annealing temperature (°C)	NH₃ flow (mL∙min⁻¹)
1 <sup>st</sup>	3	425	100
	5	450	
	7	475	
		525	
2 <sup>nd</sup>	3	425	70
	5		125
	7		

Table S2: Conditions to optimize the synthesis of Ta<sub>3</sub>N<sub>5</sub> photoelectrodes by EPD.

## 7. SEM images for the remain conditions

Figure S5 shows the top surface images from the remain best-performed optimization conditions presented in the manuscript.



Figure S5: SEM top surface images for the remain best-performed optimization conditions presented in the manuscript: a) 450-7; b) 450-5; c) 475-5.

#### 8. Annealing setup

Figure S6 shows the annealing setup where samples were placed under a NH<sub>3</sub> atmosphere. The lab facility available at LEPABE consists of an automated experimental setup – Figure S5a) ensuring a controlled environment under reproducible conditions – Figure S5b), installed inside a fume hood to ensure security gas exhaustion, which was modified with a gas/cable inlet-outlet. Three thermocouples are used to control the temperature along a 30 cm mullite tube section corresponding to the hot zone, with  $55 \times 46 \times 750$  mm dimensions (external diameter × internal diameter × length). Each extremity of the tube has a metal flange, each one connected to the gas inlet other one to the exhaust tube. A controlled and unidirectional NH<sub>3</sub> flow is kept along the mullite tube during each annealing/nitrification process, ensured by using Mass Flow Controllers (MFCs) as well as unidirectional valves, recording the gas flow conditions over time. A schematic of the sample position along the alumina tube is shown in Figure S5c).



Figure S6: Annealing setup: a) real picture of the facility; b) oven equipped with an alumina tube, under a controlled atmosphere installed inside a fume hood to ensure security gases exhaustion, which was modified with a gas/cable inlet-outlet and an NH<sub>3</sub> bottle; c) samples position over a glass holder placed into the alumina tube.

### 9. EIS measurements: bulk capacitance (C<sub>Bulk</sub>)

Figure S7 shows the bulk capacitance ( $C_{\text{Bulk}}$ ) for the four best-performed photoelectrodes and respective conditions. It should be noted that a higher charge accumulation is observed at lower potentials for samples 450-5, 450-7, and 475-5, decreasing until 0.8 V<sub>RHE</sub>; after that potential, it remained constant. In the case of sample 425-5,  $C_{\text{Bulk}}$  keeps more constant, suggesting that it is the less resistive sample from the point of view of charge transfer from the bulk to the interface, which justifies the better photocurrent registered.



Figure S7:  $C_{\text{Bulk}}$  obtained from fitting the EIS data under illumination for the Ta<sub>3</sub>N<sub>5</sub> best-performed photoelectrodes: 425 °C, 7 min (sample 425-7); 450 °C, 7 min (sample 450-7); 450 °C, 5 min (sample 450-5); 475 °C, 5 min (sample 475-5), using 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> in 1 M KOH as electrolyte solution.

## **10.** *J-E* curves of the photoelectrode and PSC assembled in the stability test

Figure S8 is important to note that the performance decreases slightly compared to that obtained in the *J-E* curves of the *Cappuccino* cell, mainly due to two reasons. The first is related to the limitations of the SRFC, since the electrical contact with the counter-electrode (carbon felt) is made through a graphite sheet glued to the cell. The graphite sheet is in direct contact with the metal to which the potentiostat wires are connected. This connection creates an increased resistance. The other reason is also related to carbon felt, which tends to be more resistive than the platinum wire that was used as a counter-electrode in the *Cappuccino* cell. When the PEC -PV arrangement was assembled, a gain of *ca*. 1.22 V was obtained, and the stability test was carried out at the potential corresponding to the maximum registered photocurrent value (0 V).



Figure S8: *J-E* curves obtained for PSC and  $Ta_3N_5$  photoelectrode covered with a ferrihydrite overlayer and  $Co_3O_4$  cocatalyst that were assembled for the stability test. *J-E* curves for  $Ta_3N_5$  photoelectrode were performed using 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> in 1 M KOH electrolyte, before and after running the 100 h stability test.

The FeOOH overlayer and the  $Co_3O_4$  co-catalyst act as a protective layer over the surface of the  $Ta_3N_5$ , as it is visible in the cross-sectional image – Figure S9. This "glue" effect seems to disappear after the aging test, although the  $Ta_3N_5$  film becomes more compact, as can be seen by SEM images before and after the stability test – Figure S9.



Figure S9: SEM top surface and cross-section images of 425-7 sample covered with protective overlayers, before and after stability test.

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