Electronic Supplementary Information (ESI)

## Highly mesoporous CsTaWO<sub>6</sub> via hard-templating for photocatalytic hydrogen production

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## Experimental



Figure S1. Scheme of the hard-templating

Sample preparation: Precursor solutions for infiltration were prepared according to literature.<sup>1</sup> 2.15 g of ethylenediaminetetraacetic acid (EDTA, Alfa Aesar, 99 %) and 2.20 g of citric acid monohydrate (Alfa Aesar, 98 %) were dissolved in 156 mL of demineralised water, the pH was adjusted to 8 using concentrated ammonium hydroxide solution (25 %). After dissolution, the pH was adjusted to 5 using concentrated nitric acid (68 %), and 10 mL of hydrogen peroxide solution (30 %) were added to stabilise the highest oxidation states of Ta and W. 1.36 g of tantalum ethoxide (Alfa Aesar, 99.999%), dissolved in abs. ethanol, were added in small portions during heating to 95 °C. Then, 823 mg of ammonium tungstate ( $(NH_4)_{10}H_2W_{12}O_{42}$ ), Alfa Aesar, 99.99%) and 655 mg of caesium nitrate (Alfa Aesar, 99.99 %) were added. The solution was evaporated until approximately 20 mL remained.

KIT-6 templates with 9 nm pores were prepared according to Kleitz *et al.*<sup>2</sup> For the synthesis of KIT-6 with 9 nm pores (BJH), 8 g of Pluronic P-123 (Aldrich) were dissolved in 240 g of demineralised water and 28.6 g of concentrated hydrochloric acid (37 %). 8 g of *n*-butanol were added at 35 °C After stirring for 1 h, 16 g of tetraethoxysilane (TEOS, VWR Chemicals) were added.

The resulting mixture was stirred for 24 h at 35 °C. The subsequent hydrothermal treatment was done for 24 h at 140 °C in a stainless steel autoclave (Parr Instrument GmbH, 450 mL), lined with a Teflon inlet. The solid product obtained was filtered, washed with demineralised water and ethanol, and dried in air at 130 °C overnight. The template was removed by calcination in air at 550 °C for 6 h, with a heating rate of 2.5 °C min<sup>-1</sup>. KIT-6 silica with 6 nm pores was prepared accordingly, except the temperature of the hydrothermal treatment was 80 °C.

<sup>&</sup>lt;sup>1</sup> L. Schwertmann, M. Wark, R. Marschall, *RSC Adv.*, 2013, **3**, 18908.

<sup>&</sup>lt;sup>2</sup> F. Kleitz, S. H. Choi, R. Ryoo, Chem. Comm, 2003, 39, 2136.

Impregnation of the template was performed by incipient wetness technique.<sup>3</sup> The amount of precursor solution for infiltration was applied according to the measured pore volumes *via* N<sub>2</sub> physisorption after each intermediate drying at 100 °C for 4 hours, in the first step being the highest.

After 5 steps of infiltration and subsequent drying, intermediate calcination was performed for 2 hours in air, at 350 °C, 400 °C or 450 °C, with a heating rate of 1 °C min<sup>-1</sup>. Afterwards, the impregnation cycle was repeated 4 times, followed by heat treatment.

The final fifth heat treatment (crystallisation) was performed at 600 °C for 4 hours in air (heating rate of 1 °C min<sup>-1</sup>). One sample (intermediate heat treatment at 400 °C) was additionally treated at 800 °C for 2 hours, to see any influence of higher temperature treatment.

To remove the silica template, etching was performed 10 times for one hour with 5M NaOH, renewing the base after each hour. Samples were washed with water until the washing water was neutral, and dried at 100 °C.

Non-porous reference CsTaWO<sub>6</sub> was prepared according to Schwertmann et al.<sup>1</sup>, and calcined at 600 °C.

*Characterisation*: X-ray diffraction (XRD) patterns were acquired using a PANalytical X'Pert Pro diffractometer with a Cu K $\alpha$  radiation source ( $\lambda = 1.5406$  Å) between  $2\theta = 10-70^{\circ}$ . The step size was set to 0.15040° and the time for one measurement was approx. 50 minutes. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 409 PC/PG instrument from 20 to 1000 °C with a heating rate of 5 °C min<sup>-1</sup> under synthetic air, and an attached mass spectrometer was detecting the evolving gases. Transmission electron microscopy (TEM) was performed using a Philips CM30 at 300 kV acceleration voltage and copper mesh grids for sample preparation. Nitrogen physisorption data were recorded with an Autosorb-6 and a Quadrasorb evo automated gas adsorption station from Quantachrome Instruments at 77 K. Specific surface areas were calculated using the Brunauer-Emmett-Teller model and pore size distributions were determined according to the BJH adsorption branch model.

*Photocatalytic Hydrogen Generation*: A mixture of 180 mL of demineralised water and 20 mL of methanol (MeOH, Roth, 99.9%) as hole scavenger was prepared and 200 mg of the respective photocatalyst was suspended in 20 mL of the solution using an ultrasonic bath for 10 min. For the photocatalytic H<sub>2</sub> generation, the resulting homogenous suspension and the remaining water/methanol mixture were filled in a glass reactor with top quartz window and a water cooling jacket. The temperature was kept constant at 20 °C throughout the reaction using a thermostat. Rhodium as a co-catalyst precursor for photodeposition was added using an aqueous sodium hexachlororhodate (Na<sub>3</sub>RhCl<sub>6</sub>, Aldrich, 99.999 %) solution. The whole suspension was stirred at 400 rpm and flushed with a continuous argon gas flow of 100 mL min<sup>-1</sup> controlled with a Bronckhorst mass flow controller to remove residual air from the reactor. After one hour, the gas flow was set to 25 mL min<sup>-1</sup> and a 150 W solar simulator (Newport Oriel Sol 1A) was turned on as light source for photocatalysis (1 sun intensity, 1000 W/m<sup>2</sup>). The AM1.5G filter was removed to get more UV light for the high band gap materials. Hydrogen evolution was measured by gas chromatography using a Shimadzu GC 2014 with a TCD detector and a Shin carbon column.

<sup>&</sup>lt;sup>3</sup> T. Wagner, S. Haffer, C. Weinberger, D. Klaus, M. Tiemann, Chem. Soc. Rev. 2013, 42, 4036.

## **Results and Discussion**



**Figure S2**: a)  $N_2$  isotherms of samples after stepwise infiltration of CsTaWO<sub>6</sub> precursor into the pores of KIT-6 ; b)  $N_2$  isotherms of the KIT-6/CsTaWO<sub>6</sub> composite after the calcination (at 600 °C) compared to the bare KIT-6.



**Figure S3**. a) XRD pattern of mesoporous CsTaWO<sub>6</sub> after 5 cycles of impregnation followed by template removal. The temperature for all calcination steps was 600 °C leading to undesired by-phases; b) respective  $N_2$  physisorption isotherms and pore size distribution of the same sample.



Figure S4. TG-MS of dried CsTaWO<sub>6</sub> sol-gel precursor solutions, non-calcined

Table S1: Textura	l data of meso	porous and c	composite n	naterials
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	BET area /	total pore volume /	pore diameter (BJH) /
	$m^2 g^{-1}$	cm <sup>3</sup> g <sup>-1</sup>	nm
KIT-6	490	1.38	9.1
CTW-350°C (after first calcination)	160	0.32	6.8
CTW-350°C (after second calcination)	160	0.31	6.8
CTW-350°C (after third calcination)	155	0.28	6.8
CTW-350°C (after fourth calcination)	145	0.24	6.8
CTW -350°C / 600°C (after fifth calcination and crystallisation at 600 °C) CTW-350°C (after silica removal)	115	0.25	7.4
	95	0.32	14.0
CTW-400°C (after first calcination)	250	0.52	7.4
CTW-400°C (after second calcination) CTW-400°C (after third calcination) CTW-400°C (after fourth calcination)	225	0.44	7.3
	190	0.34	6.8
	170	0.29	6.8
CTW-400°C/ 600°C (after fifth calcination and crystallisation at 600 °C)	105	0.23	6.9

CTW-400°C / 600°C / 800 °C (after additional 800°C)	35	0.21	18.6	
CTW-400°C / 600°C (after silica removal)	105	0.35	~15	
CTW-400°C / 600°C / 800 °C (after silica removal)	85	0.33	~20	
CTW-450°C				
(after first calcination)	265	0.54	6.4	
CTW-450°C	190	0.38	61	
(after second calcination)	170	0.50	0.1	
CTW-450°C	165	0.31	5.8	
(after tind calcination) CTW-450°C				
(after fourth calcination)	145	0.26	5.5	
CTW -450°C / 600°C				
(after fifth calcination and	100	0.23	6.5	
crystallisation at 600 °C)				
CTW-450°C / 600°C	115	0.32	12	
(after silica removal)				



**Figure S5**. a) Sequential pore filling of KIT-6-140 with CsTaWO<sub>6</sub> by five cycles of impregnation and calcination at 350 °C (600 °C for the last cycle), followed by  $N_2$  physisorption; b) respective XRD patterns after each cycle.



**Figure S6**. a) Sequential pore filling of KIT-6-140 with CsTaWO<sub>6</sub> by five cycles of impregnation and calcination at 450 °C (600 °C for the last cycle), followed by  $N_2$  physisorption; b) respective XRD patterns after each cycle.



Figure S7. High magnification of mesoporous crystalline CsTaWO<sub>6</sub> after 450 / 600 °C preparation.



Figure S8. HRTEM images and SAED of mesoporous crystalline CsTaWO<sub>6</sub> after 400 / 600 / 800  $^{\circ}$ C preparation

	From (511) reflection	From (440) reflection	
	nm	nm	
350 °C / 600 °C	13	13	
400 °C / 600 °C	10	10	
450 °C / 600 °C	10	10	
400 °C / 600 °C / 800 °C	12	11	

**Table S2**: Crystallite size from integral width after calcination and template removal



**Figure S9**. UV-Vis diffuse reflectance spectra of mesoporous CsTaWO<sub>6</sub> samples compared to the non-porous reference.



**Figure S10**. XRD patterns of the resulting powder after hard-templating inside KIT-6 with 6 nm pore size (KIT-6-80).