Novel synthesis route of plasmonic CuS quantum dots as efficient co-catalysts to TiO_2/Ti for light assisted water splitting

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Supporting information

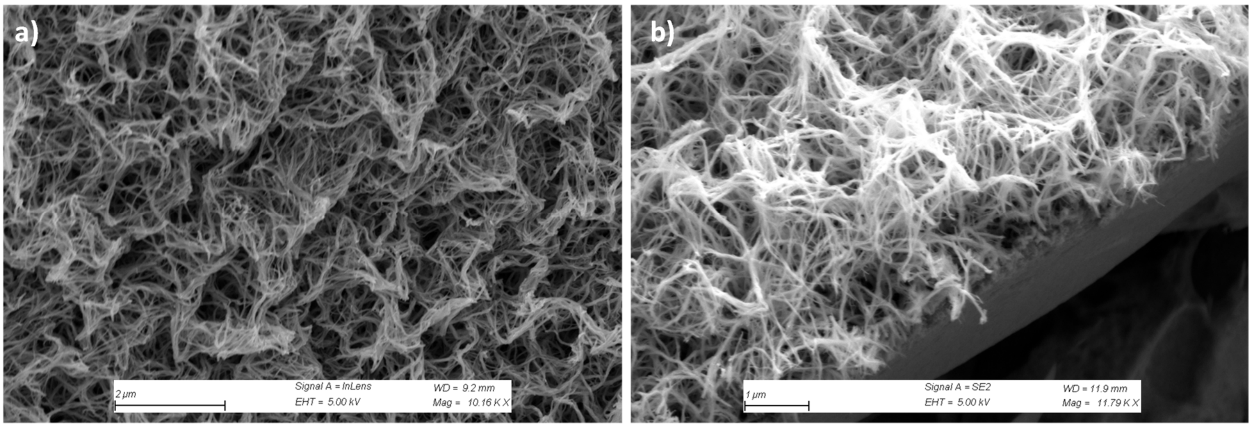

Figure S1. SEM **a)** top view and **b)** cross view of the as prepared TiO_2/Ti sheet confirming the 1D morphology of the formed titania, covering all the Ti substrate surface.

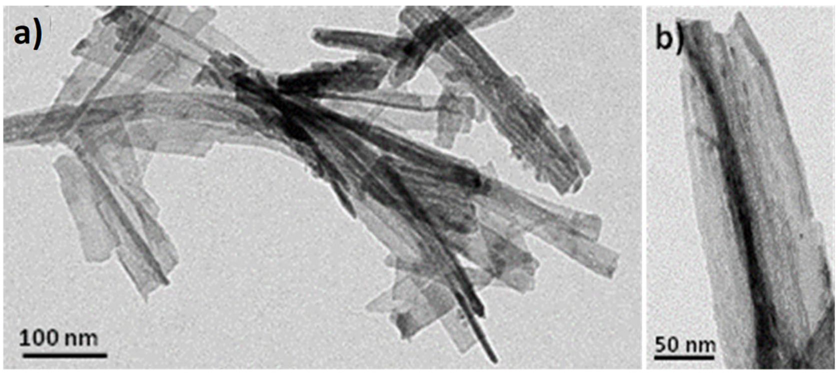

Figure S2. TEM micrographs recorded on **a)** an assembly and **b)** an individual representative TiO_2 NFs separated by sonication from the as-produced TiO_2/Ti sheets in an ethanolic solution. Titania fibers appear as veils folded on themselves.

CuS reference	MW Power (W)	MW Heating time (min)	Sulfur source
CuS-ThU-1200-1	1200	1	ThU
CuS-ThU-1200-3	1200	3	
CuS-ThU-200-25	200	25	
CuS-TAA-1200-1	1200	1	TAA
CuS-TAA-1200-3	1200	3	
CuS-TAA-200-25	200	25	

Table S1. List of prepared CuS samples and their main synthesis MW-assisted polyol synthesis

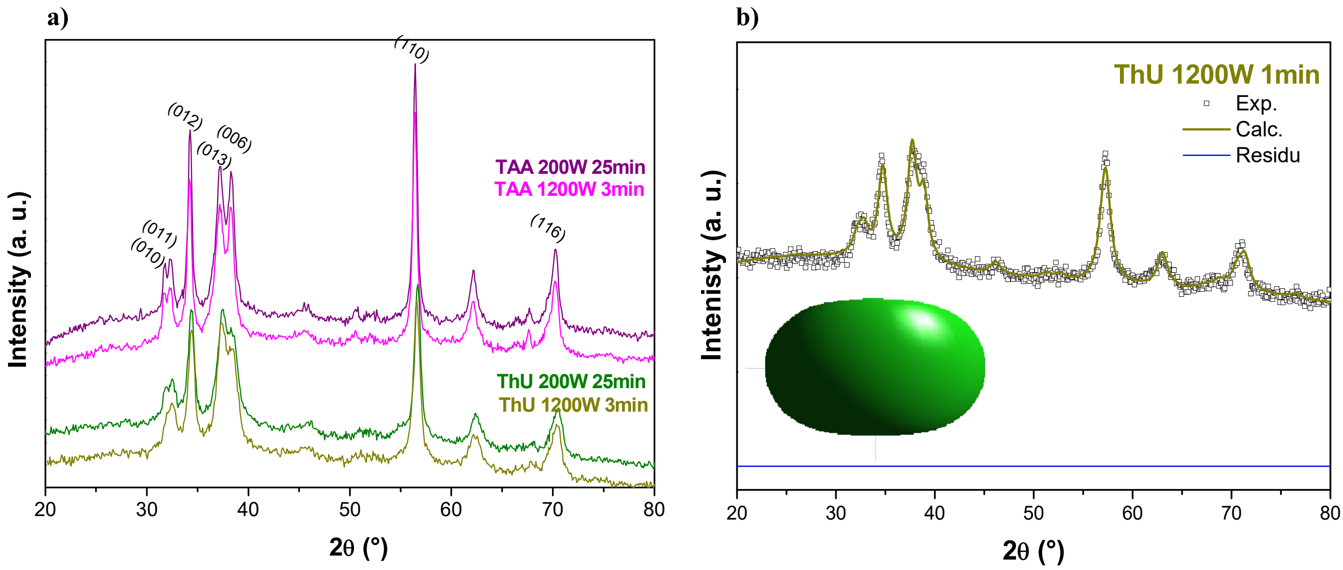

Figure S3. **a)** XRD patterns of CuS particles prepared using TAA (up) and ThU (bottom) reagents while applying a microwave heating power of 200 and 1200 W for a total reaction time of 25 and 3 min, respectively. **b)** Results of Rietveld refinements (using MAUD software [1]performed on the XRD pattern of CuS-ThU-1200-1 particles to illustrate the quality of the fits: the experimental pattern (black scatter) and the calculated one (green line) are perfectly superposed with a residue curve, defined as the difference between the experimental and calculated diffractograms, close to zero (blue line). The inferred crystallite shape is also given for information.

	R_{wp} (%)	R_B (%)	R_{exp} (%)	a (Å) ± 0.005	c (Å) ± 0.005	$L_{[006]}$ (nm) ± 0.5	$L_{[100]}$ (nm) ± 0.5
TAA 200W 25min	1.57	1.10	0,79	3.789	16,386	12.2	19.1
TAA 1200W 3min	1.64	1.13	0.83	3.789	16,366	12.1	14.9
TAA 1200W 1min	1.70	1.33	1.13	3.786	16,306	10.1	13.0
ThU 200W 25min	1.52	1,06	0.82	3.787	16,324	9.9	11.6
ThU 1200W 3min	1.40	1.00	0.80	3.791	16,386	9.9	10.8
ThU 1200W 1min	1.66	1.29	1.15	3.780	16,309	7.8	7.7
Covellite CuS standard (ICDD N°98-004-1975)				3.796	16.360	-	-

Table S2. Main Rietveld refined structural parameters and their related reliability fit factors. The overall fit quality is described by a weighted profile (R_{wp}), expected profile (R_{exp}) and Bragg R-value (R_B) close to 1, which is the case here.

[1] L. Lutterotti, S. Matthies, H. R. Wenk, MAUD: a friendly Java program for material analysis using diffraction, *IUCr: Newsletter of the Commission on Powder diffraction*, **1999**, *21*, 14-15.

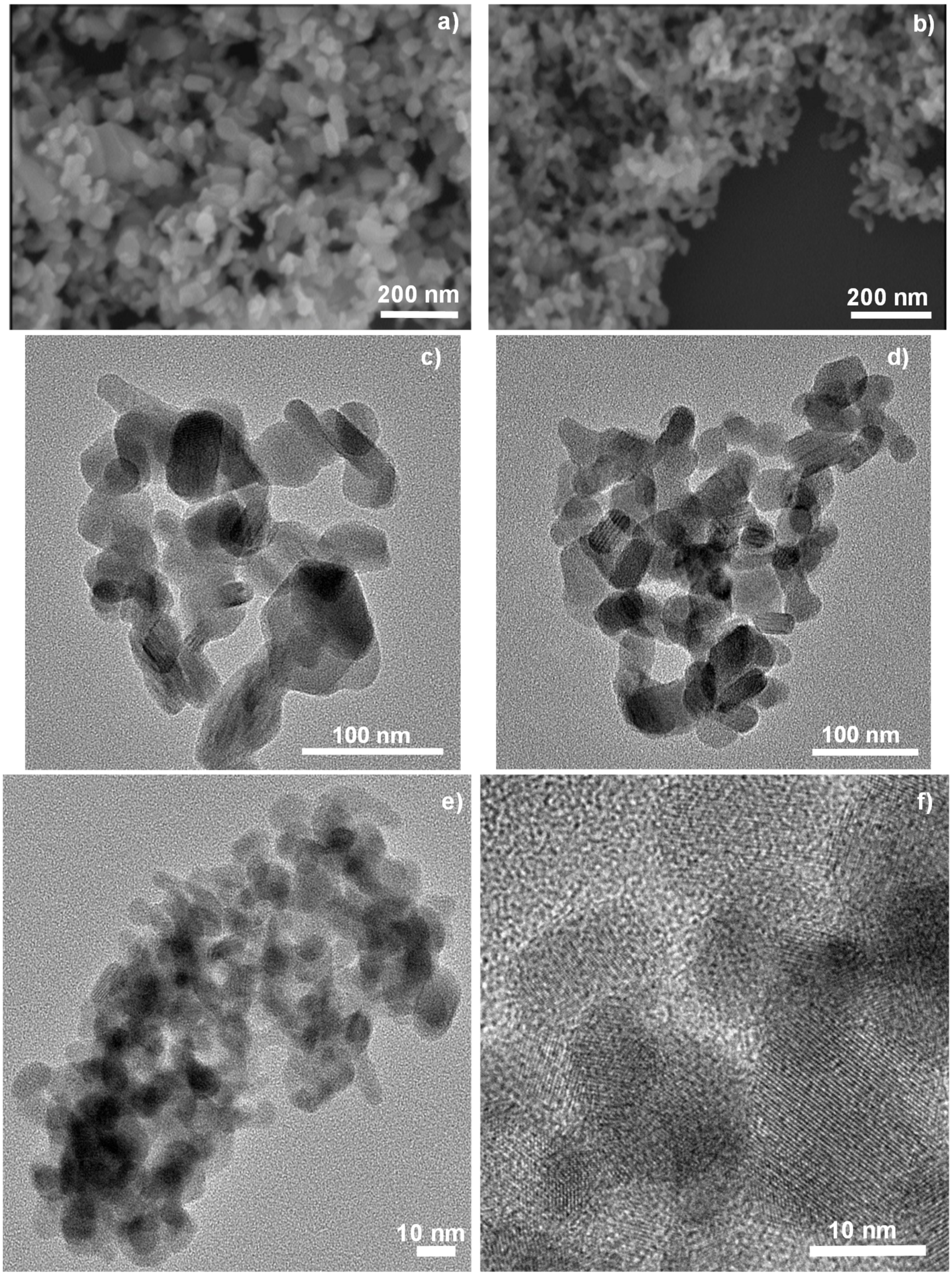

Figure S4. SEM images recorded on **a)** CuS-TAA-200-25 and **b)** CuS-ThU-200-25 particles. TEM images of **c)** CuS-TAA61200-3 and **d)** CuS-1200-ThU-1200-3 particles. **e)** TEM micrograph of CuS-ThU-1200-1 particles and **f)** HRTEM image of some representative CuS-ThU-1200-1 particles.

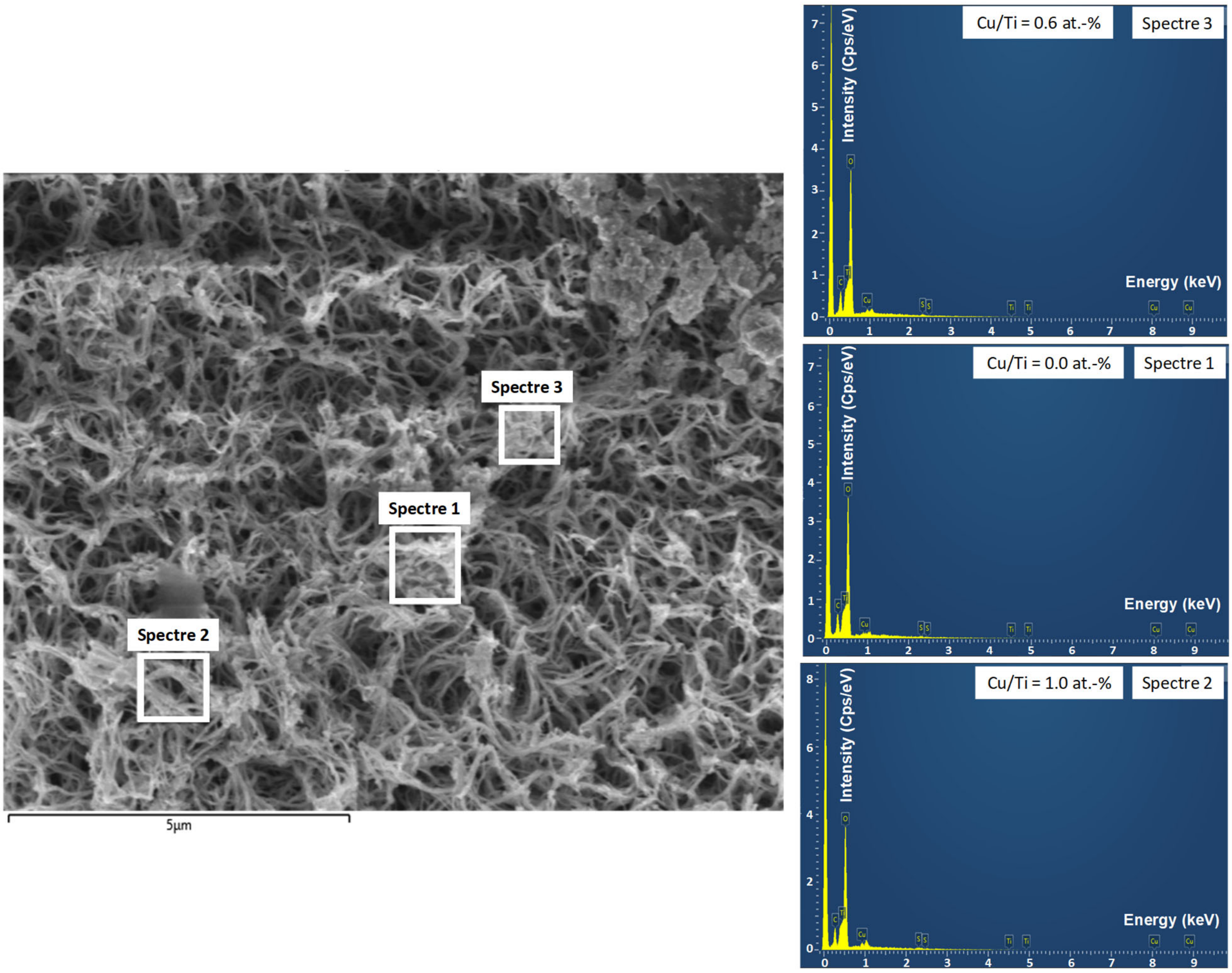

Figure S5. SEM-EDS analysis of CuS-TiO_2/Ti, focusing on TiO_2 fibers nodes, where CuS particles seem to accumulate, leading to an average Cu/Ti atomic ratio of 0.5 at.-%.

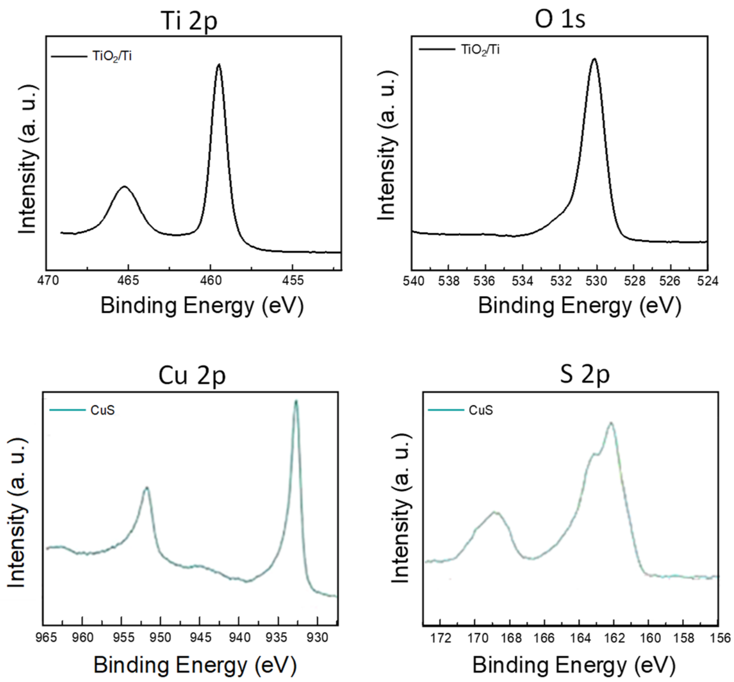

Figure S6. Ti 2p and O 1s high resolution XPS spectra recorded on pristine TiO_2/Ti (black) and Cu2P and S 2p high resolution XPS spectra recorded on pristine CuS (blue-green line).

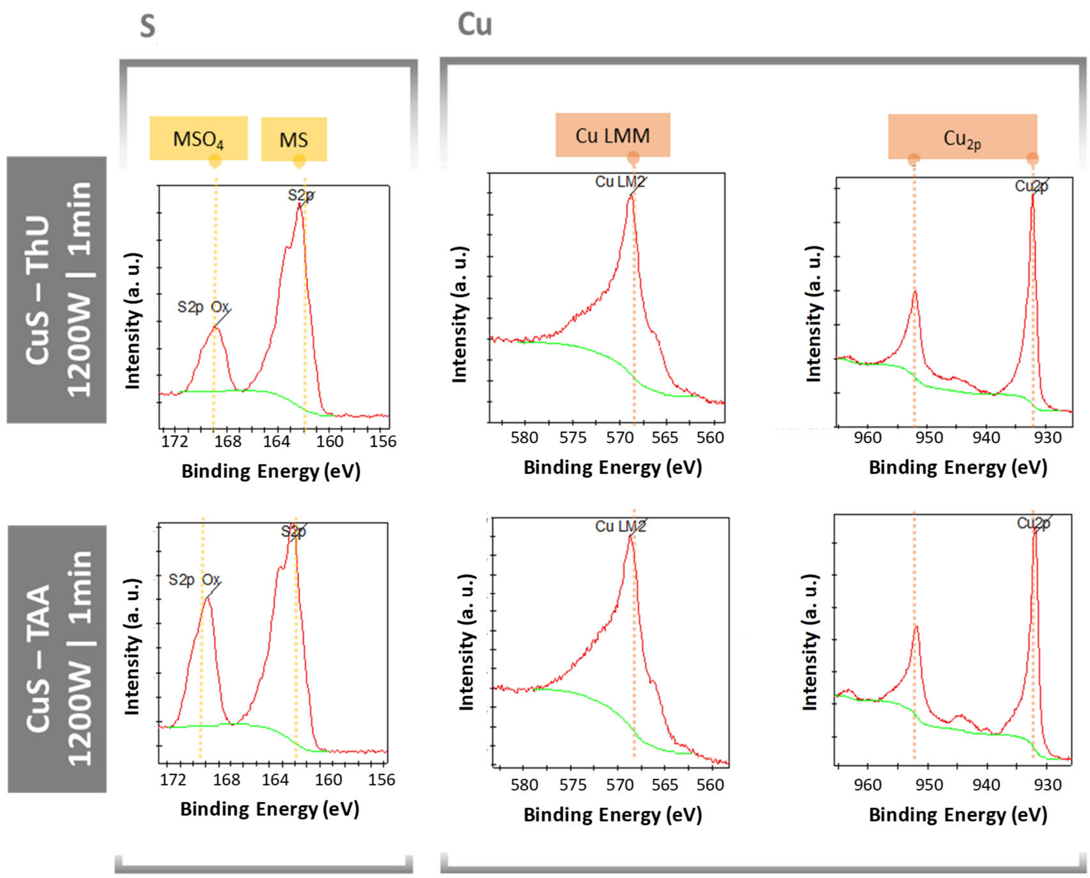

Figure S7. S 2p, Cu 2p and Cu LMM high resolution XPS spectra recorded on CuS NPs produced using ThU or TAA sulfur source for a microwave heating power of 1200 W along 1 min of reaction time.

Composite	Synthesis method	Electrolyte	Light source	Photocurrent density (mA/cm^2)	Ref
CuS/TiO_2 nanocomposites	Co-precipitation	0.1 M Na_2SO_4	UV-LED lamp (25 W, 365 nm)	0.2 (at 0.6V *vs.* Ag/AgCl)	[2]
CuS/TiO_2 nanocomposites	Hydrothermal	0.1 M Na_2SO_4	UV-LED lamp (25 W, 365 nm)	0.17 at 0.6V *vs.* Ag/AgCl	[2]
CuS nanoflakes/TiO_2 Nanospindles	hydrothermal and solution-based process	0.5 M Na_2SO_4	Xe arc lamp (300 W)	0.12 (at 0.6V *vs.* SCE)	[3]
TiO_2/CuS nanowire array heterostructures	SILAR method	1 M Na_2SO_4	AM 1.5G sunlight simulator (100 mW/cm^2)	0.063 (at 0V *vs.* Ag/AgCl)	[4]
TiO_2@CuS double-shell nanoboxes	constructed via a multistep control strategy	0.35 M Na_2S + 0.25 M Na_2SO_3	chopped illumination *of* simulated sunlight	0.032 (at 0V *vs.* Ag/AgCl)	[5]
TiO_2/CuS core-shell nanorods	CuS(*n*) shell produced by ion exchange from ZnS(*n*) counterparts prepared by SILAR route	–	AM 1.5G sunlight simulator (100 mW/cm^2)	3.32 (at 0V *vs.* Ag/AgCl)	[6]
CuS-TiO_2 composite	Electrophoretic deposition	0.50 M CH_3OH as electroactive species in Na_2CO_3/$NaHCO_3$ (pH = 9.5)	Visible light irradiation	0.3 (at 0V *vs.* SCE)	[7]
CuS-TiO_2 core-shell structure	Hydrothermal method	0.1 M PBS and 0.1 M KCl	Xe lamp with a 400 nm cut-off filter	0.0054 (at 0.1V *vs.* Ag/AgCl)	[8]
CuS/TiO_2(NTs)	SILAR method	0.1 M PBS and 10 mM glucose	Xe lamp (400 W)	0.0118 (at 0V *vs.* Ag/AgCl)	[9]
CuS/TiO_2	Wet impregnation	3.5 wt.-% NaCl in water	Hg-Xe lamp UV with a 365 nm band-pass filter (1 mW/cm^2)	9.3 (at 0V *vs.* Ag/AgCl)	[10]
CuS-TiO_2	*in situ* chemical bath deposition	–	AM 1.5G sunlight simulator (100 mW/cm^2)	4.5 (at 1V *vs.* Ag/AgCl)	[11]
CuS-TiO_2(NFs)	Ethanolic impregnation	0.5 M Na_2SO_4 (pH = 7.0)	Xeon lamp (150 W)	0.030 (at 0V *vs.* SCE) 0.122 (at 1.23V *vs.* SCE)	(*)

(*) This work

Table S3. Comparison of the PEC performances of our engineered photoanode with those of CuS-TiO_2 based literature.

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[4] S. Jia, X. Li, B. Zhang, J. Yang, S. Zhang, S. Li, Z. Zhang, TiO_2/CuS heterostructure nanowire array photoanodes toward water oxidation: The role of CuS, *Appl. Surf. Sci*., **2019**, *463*, 829-837.

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